FLAME RETARDANT NATURAL FIBRE COMPOSITES FOR HIGH PERFORMANCE APPLICATIONS

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DECLARATION OF AUTHORSHIP

I declare that the works described in this PhD dissertation has not been previously presented in any form to the University or to any other institutional body, whether for assessment or for other purposes. I confirm that the intellectual content of the work is the result of my own original research and of no other person.

Signed ……..

Date ……..…..

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Abstract

Natural fibres such as flax, jute and hemp are becoming attractive alternatives to traditional high performance fibres such as glass and carbon fibres for reinforcement in composites. This is because natural fibres are from renewable sources, are biodegradable, and therefore are more environmentally friendly. However, unlike inherently non-flammable glass and carbon fibres, natural fibres thermally degrade and burn readily and their use has been restricted in applications where the fire regulations are stringent. In addition, natural fibres have low compatibility with a polymer matrix, especially hydrophobic polymers such as polypropylene, causing poor fibre/matrix interfacial adhesion in composites. This leads to lower mechanical performance in natural fibre composites. Therefore treatments/modifications of fibre and/or polymer matrix are required to overcome these drawbacks and expand their range of applications.

The main aim of this PhD is to develop flame retardant (FR) natural fibre composites for high performance applications by using FR treated fibres and/or polymer matrices with FR treatment. To achieve this, firstly the flammability of different natural fibres and bio/synthetic polymers was studied by using limiting oxygen index (LOI) and cone calorimetry to identify suitable components for producing FR natural fibre composites. Flax was selected as reinforcing component, and three polymers (polypropylene (PP), polylactic acid (PLA) and poly(furfuryl alcohol) (furan resin)) were selected for polymer matrices. Various strategies to develop flame retardant natural fibre composites were adopted. These can be summarised as (1) development of FR composites from FR treated flax/PP and flax/PLA commingled, woven fabrics, (2) surface modification of flax/PP and flax/PLA fabrics for improving fibre-matrix adhesion in FR composites, (3) development of FR bio/synthetic polymer matrix, and (4) Identification of suitable FR strategy involving synergistic combination of different FR components for producing high performance FR natural fibre composites. The fire performance of these natural fibre composites was evaluated by using UL-94 and cone calorimetry, while the mechanical performance was studied by tensile, flexural testing.

In order to develop flame retardant flax/PP and flax/PLA composites from commingled flax/PP and flax/PLA woven fabrics, it was established that the best way to render these flame retardant is to apply FR aqueous solutions by using a conventional pad-dry technique, commonly used for textiles. Usually for textile finishes, fabrics are first scoured which helps in improving the pickup of fabrics. As a first step, the effect of fabric pre-treatment (scouring) on fire and mechanical performance of composites was studied. It was concluded that there is no advantage of using an extra process of scouring during FR composite preparation as the improvement in fire and mechanical properties were only marginal. A number of commercially available water soluble flame retardants were used, out of which guanylurea methylphosphonate (GUP), was seen to be the most effective FR to

improve fire performance of the composites. However, GUP caused significant reduction in mechanical properties of the composites therefore the effect of flame retardant concentration on fire and mechanical performance of the composites was studied in order to identify an optimised flame retardant formulation that significantly improves fire retardancy (i.e. V-0 rating in UL-94) of each of flax/PP and flax/PLA laminates with minimal effect on their mechanical performances. The optimised GUP content for flax/PP and flax/PLA was identified as those which have respectively 0.9% and 0.6% phosphorus in respective fabric/composite. To improve fibre/matrix interfacial adhesion in these composites, different surface modification treatments of the fabrics were studied including silane solution application (i.e. triethoxyvinylsilane (VTS) and 3-aminopropyl triethoxysilane (APS) for flax/PP and flax/PLA respectively), exposure to atmospheric argon-plasma and a combination of both. The fibre/matrix interfacial adhesions of these composites were studied by using peeling and flexural tests. The results showed that the combination of plasma and silane treatments was the most effective method to improve the fibre/matrix adhesion for FR treated flax/PP, whereas only plasma treatment was required for FR flax/PLA composites.

In order to develop flame retardant polymer matrices, PP and PLA were compounded with different flame retardants and then extruded into fibres. The commercially available organic phosphorus compound (OP) was seen to be the most effective FR to improve flammability of PP and PLA fibres. In furan resin also a number phosphorus based FRs were studied, from which ammonium polyphosphate (APP) and melamine polyphosphate (MPP) were seen to be most effective.

These FR components were then used in different combination (i.e. either application of FR on flax, or in polymer matrix, or both) in order to identify the most effective FR strategy to improve fire performance of a composite with minimum effect on mechanical properties. For FR thermoplastic (flax/PP and flax/PLA) composites best results were achieved with the use of FRs in both flax fibre and polymer matrix. On the other hand for FR flax/furan laminates, the addition of FR in the resin provided best results.

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Chapter 1: Introduction

1.1 Composites and natural fibre composites

High strength, low density, low cost and durability of composite materials are the factors responsible for their wide spread usage and replacement of metallic components in structural applications [1,2]. For the last 30 years or so, glass, carbon, and aramid fibres have dominated the composite industry, mainly due to their excellent thermo mechanical properties [1,2]. Polymeric matrices of choice have been epoxy, unsaturated polyester, and vinyl ester, mainly because of their good mechanical properties, hydrophobicity, and resistance to chemicals [1]. In more recent years, thermoplastic composites have gained importance in manufacturing industries, particularly automotive, construction and packaging. Environmental requirements and new regulations on the recyclability of composites urged the researchers to develop materials from renewable sources. Natural fibres such as flax, hemp, sisal, jute, bamboo, etc. fit some of the required criteria, i.e. they are from renewable sources, are naturally biodegradable, have low density, high specific strength and modulus, and are economical to use [3-9]. However, these fibres have certain disadvantages such as the variable quality of the fibres owing to their origin and from crop to crop, hydrophilicity, and low strength [3-6,9].

Natural fibres, in particular cellulosic fibres, theoretically have a high elastic modulus, 138 GPa [10], but the presence of defects in their morphology result in low strength in comparison with existing synthetic fibre reinforcement. Moreover, the hydrophilic characteristic of natural fibres causes poor compatibility with polymer matrices, especially hydrophobic polymers such as polyethylene (PE) and polypropylene (PP), and hence results in a lower mechanical performance of natural fibre composites than the expected values [3-5]. Natural fibre composites have lower mechanical properties as compared to the conventional fibre reinforced composites. Hence, the use of natural fibres in composites is mainly restricted to semi-structural applications such as seatbacks, parcel shelves, and door liners in automotives [6].

Another drawback of natural fibres is their higher flammability as compared to the existing reinforcement fibres such as glass and carbon fibres. A replacement of glass and carbon fibres in composites with natural fibres leads to an increase in flammable components, and so results in more flammable composites. This restricts their usage as reinforcement for composites in many applications, especially where the fire regulations are stringent [9].

Natural fibres can be used with thermoplastic, thermoset or biopolymers as long as processing temperature of the polymer is lower than the onset of decomposition temperature of the natural fibre. Various natural fibres-polymer matrix combination reported in literatures are summarised in Table 1.1.

Table 1.1: Reported natural fibre – polymer matrix combinations used for fabricating composites (taken from Ref [4] and [9])

Natural fibres	Polymer matrices		
	Thermoplastic	Thermoset	Biopolymer
Cellulose	PP, PE, PA66, PVC, PS	EP, UP	PLA, PHBV
Jute	PP, PE	EP, UP, VE, Ph, Acrylic, PET	PLA, PHBV
Flax	PP, PE	EP, UP, VE, Ph, Acrylic, Melamine	PLA, PGA, PHB, PCL
Sisal	PP, PE, PS	EP, UP, PET	-
Abaca	PP, PE	EP, UP	PLA, PHBV
Kenaf	PP, PE	EP, UP, Ph	PLA
Ramie	PP	EP, UP	PLA, PCL
Hemp	PP, PE	EP, UP, VE, Ph	-
Coir	PP	EP, UP	-
Bamboo	PP	EP, UP	PCL
Banana	-	UP, Ph	-
Pineapple	PE	UP, Ph	-
Sun hemp	PP	UP	-
Wheat straw	PP, PE	UP	-
Wood flour/fibre	PP, PE, PVC, PS, PU	UP, PET	-
Wool		PET	-

Note: PP = Polypropylene; PE = polyethylene; PA66 = polyamide 6,6; PVC = polyvinyl chloride; PS = polystyrene; PU = polyurethane; EP = epoxy; UP = unsaturated polyester; VE = vinyl ester; Ph = phenolic; PET = polyester; PLA = polylactic acid; PGA = polyglycolic acid; PHBV = poly(3-hydroxybutyrate-co-3-hydroxyvarelate); PHB = polyhydroxybutyrate; PCL = poly-ε-caprolactone.

The most widely used thermoplastic matrix is polypropylene (PP), mainly due to the suitable processing temperature (160 – 180^{o}C), and good mechanical, electrical and chemical properties [9]. Among thermoset polymers, unsaturated polyester and low temperature curing epoxies are also widely used. Since 1990s there has been considerable interest in biodegradable polymeric matrices. Polylactic acid (PLA) is one of such polymer with good mechanical properties. Other biopolymers will be discussed in details in *Chapter 2*. The combination of biodegradable natural fibre and biodegradable polymer matrix leads to a fully biodegradable composites. The challenge of successfully using natural fibre composites as replacement for of glass/carbon fibre-reinforced composites is to compete on physical, mechanical and thermal properties.

1.2 Composite types used in various applications

Composites are used in transport: aerospace, marine, rail, automotive; and construction industries. The choice of a particular composite type for a particular application is mainly based on its mechanical, physical and chemical properties. In marine applications, composites are widely used in primary structures of ship such as hull, decks, structural bulkheads, etc. The commonly used composite systems are glass reinforced unsaturated polyester and vinyl esters due to their excellent mechanical properties; high chemical and corrosion resistance [1,2,11]. Railways and automotives increasingly are using glass fibre reinforced polyester and vinyl ester composites for the structural parts such as body frames and structures [11]. Besides, unsaturated polyester and vinyl ester composites, thermoplastic composites, i.e. glass and natural fibres reinforced polypropylene, are also used in automotive industry for non- and semi-

structural components, i.e. door panels, roof trim panels, load floors and battery trays, as these do not require high mechanical performance materials [2,6,9]. In aerospace, composites are used in various parts such as doors, control surfaces, wing boxes, sidewalls, ceiling and bulkheads [1,2]. Materials used in aerospace generally require very high mechanical performance in comparison to other applications, hence carbon fibre reinforced epoxy, in particular multifunctional (tri- of tetra- functional) type of epoxy resin, is the most commonly used system due to its superior mechanical performance.

1.3 Fire performance requirements for different application areas

In order to use polymer based materials for commercial applications such as transport and construction sector, they have to conform to certain regulations for a particular area as discussed below [12].

Automotive

The fire performance required for materials used for automotive applications is specified in Federal Motor Vehicle Safety Standard No. 302 (FMVSS 302) in United State which is virtually an international standard. Some other equivalent standards in other countries include BS AU 169 (United Kingdom), ST 18-502 (France), DIN 75200 (Germany), and JIS D 1201 (Japan) [13,14]. For FMVSS 302, horizontal rate of burning of materials (356 mm x 100 mm x ~nominal thickness) when ignited with a 38 mm high flame for 15 s is determined, and this should not exceed 102 mm/min in order to pass the requirement as specified in the standard [13].

Railway

The fire regulations of railways are much more stringent than those for automotives due to the limitations of escape in the case of fire, particularly for underground trains. The fire testing standards of materials used for railways vary from country to country. In United Kingdom, the standard for materials used in British railways is given in BS 6853 [15]. To pass the requirement of BS 6853, materials are required to have low fire propagation rate, smoke production and toxicity. One of the most important flammability testing specified in BS 6853 is the surface flame spread test where materials of 885 mm x 270 mm x ~nominal thickness up to 50 mm are mounted vertically and exposed to a radiation panel of 32.5 kW/m^2 heat flux and ignited with a pilot flame at the bottom of the exposed edge for 1 min as described in BS 476 Part 7 [16]. The flame spread results are taken at 1.5 min and at the end of the test, which must not exceed 215 mm and 455 mm, respectively, in order to pass the requirement [15].

Marine

The fire performance requirement of materials for passenger and cargo ships are specified as IMO/HSC Code (Code of Safety for High Speed Craft of the International Maritime

Organization) in the International Convention for the Safety of Life at Sea (SOLAS) [17,18]. The testing procedures used to access the flammability of materials as specified in the standard are described in ISO 9705 and ISO 5660 for room/corner and cone calorimetric tests respectively [19,20]. According to ISO 9705 the interior of the fire test room is covered with the testing material, and ignited with a pilot flame of 100 kW for 10 min and thereafter at 300 kW heat output for 10 min [19]. During the test, the change of heat output at the burner is measured for heat release rate of the specimen. ISO 5660 measures the heat release rate of the materials from a specimen, 100 mm x 100 mm, mounted horizontally, and exposed to 50 kW/m^2 external heat flux of cone calorimeter in the presence of a spark ignition [20]. The average and peak of heat release rates of materials in these tests must be lower than 500 kW and 100 kW respectively, in order to pass the requirement of the standards.

Aviation

For aerospace applications, the composites used for the interior parts in aircraft are required to comply with the US Federal Aviation Regulation (FAR). One of the flammability tests for evaluating the fire performance of materials specified in the regulation is the heat release rate test where a specimen of 150 mm^2 surface area is tested at 35 kW/m^2 external heat flux in a Ohio State University calorimeter [21]. The peak of heat release rate and total heat released over first 2min are measured, and must be lower than 65 kW/m^2 in order to pass the requirement of the regulation.

Construction

There is no international fire safety standard for construction, and most of the countries have their own standards, which can vary from country to country [12]. On the other hand, European countries have established their own fire regulations for materials used in construction as EN 13501-1 [22]. A number of the standard testing procedures are specified in EN 13501-1 to determine the reaction to fire of materials such as heat of combustion test (EN ISO 1716), single burning item test (EN 138230), ignitibility and flame spread test (EN ISO 11925-2) [22]. These tests are used for evaluating fire performance of materials in term of heat release rate, rate of flame spread, smoke production, and toxicity of effluent produced during combustion of materials from the ignition to flashover stages of fire [12]. To pass the requirement of the regulation materials are required to have low total heat release, rate of flame spread and smoke production, and in some applications such as ceiling the production of flaming droplets is also limited.

1.4 Mechanical and fire properties of different composites

In order to understand why certain composites are used at present in certain applications, the mechanical and fire properties of different types of composites are compiled in Table 1.2. These values are taken from previous works done at University of Bolton or from literature.

Table 1.2: Reported flammability and mechanical properties of different types of composites [23-30]

Composites	Fibre/resin composition (wt%/wt%)	Thickness (mm)	Cone calorimetric results					UL-94 Vertical rating	Flexural modulus (GPa)	Tensile modulus (GPa)
			Heat flux used (kW/m^2)	TTI (s)	PHRR (kW/m^2)	THR (MJ/m^2)	TSR (L)			
Carbon/EP-H [23]	67/33	3.0	50	64	224	19	1404	NR	43.2	85.1
Glass/EP-H [24]	55/45	2.0	50	42	385	22	908	NR	21.0	24.8
Glass/EP-L [25]	50/50	2.8	50	44	456	38	1508	NR	15.4	15.8
Glass/UP [26]	40/60	3.0	50	33	440	42	1568	NR	12.7	16.9
Glass/Phenolic [27]	40/60	4.5	50	164	110	25	336	V-0	10.4	13.5
Glass/Furan [28]	42/58	4.0	50	191	174	17	22	V-0	9.0	7.7
Glass/PP [29]	40/60	3.5	35	25	506	80	1308	NR	6.6	9.8
Flax/EP-L [30]	45/55	4.4	50	35	616	96	3038	NR	10.0	8.8
Flax/PP	50/50	2.8	35	31	452	98	970	NR	7.0	6.4
Flax/PLA	50/50	2.8	35	34	313	58	159	NR	13.7	9.0

Note: EP-H and EP-L represent high (tri- and tetra-) and low (bi-) functional epoxies respectively

Carbon fibre reinforced epoxy composite (Carbon/EP-H), which is widely used in aerospace, shows excellent mechanical properties of 43.2 GPa flexural modulus and 85.1 GPa tensile modulus. This composite was prepared by the prepreging technique, hence has low resin content (33 wt-%) as compared to other composites. This Carbon/EP-H also exhibits high fire performance as can be seen from cone calorimetric results tested at 50 kW/m^2. Carbon/EP-H ignited at 64 s and burned with relatively low peak of heat release rate (PHRR) of 224 kW/m^2 producing total heat release (THR) of 19 MJ/m^2 and total smoke (TSR) of 1404 L. However, Carbon/EP-H could not pass the criteria of vertical rating in UL-94 test, and termed as no rating (NR) as shown in Table 1.2.

Glass fibre reinforced high functional epoxy composite (Glass/EP-H) shows the flexural and tensile modulus of 21.0 GPa and 24.8 GPa, respectively, which are lower than that of Carbon/EP-H. This is due to the lower mechanical properties of glass in comparison to carbon fibre, and also the low fibre content in Glass/EP-H as compared to that of Carbon/EP-H, resulting in lower mechanical properties of Glass/EP-H (Table 1.2), particularly tensile properties, which are fibre dependent. For the fire performance, the results show that Glass/EP-H is more flammable than Carbon/EP-H as can be seen from the cone test results it ignited at 42 s and burned with higher PHRR and THR of 385 kW/m^2 and 22 MJ/m^2 respectively. It is to be noted that the resin content in Glass/EP-H is higher than Carbon/EP-H (Table 1.2), hence could be the reason of the higher flammability of Glass/EP-H, moreover both resins are of different grades. In UL-94 Glass/EP-H failed the vertical rating test. The use of another type of epoxy resin, with lower functionality and curing temperature (EP-L) as polymer matrix, the flexural and tensile moduli of Glass/EP-L are 15.4 GPa and 15.8 GPa, respectively, which are lower than Glass/EP-H. The cone calorimetric results show that the time-to-ignition (TTI) of Glass/EP-H and Glass/EP-L are similar, but the PHRR and THR of Glass/EP-L are higher, Table 1.2. Glass/EP-L also produces high volume of smoke of 1508 L during burning. These results indicate that the mechanical and fire performance of glass fibre reinforced composites are lower when using epoxy resin with low functionality than when using one with high functionality. Glass reinforced unsaturated polyester composites (Glass/UP) shows the mechanical performance of 12.7 GPa flexural modulus and 16.9 GPa tensile modulus. Flexural modulus is matrix dependent, which is lower here, whereas the tensile being fibre dependent is similar to the glass reinforced epoxy composites. Small variations though are due to the different resin/fibre content in these two types of composites (see Table 1.2). Cone calorimetric results show that Glass/UP ignited at 33 s, and burned with PHRR of 440 kW/m^2, producing 42 MJ/m^2 THR and 1568 L TSR. Glass/UP also failed to rate in vertical rating of UL-94. These properties are similar to that of the EP-L epoxy. For glass reinforced phenolic composite (Glass/Phenolic), the mechanical properties are lower than for the other composites discussed above, as can be seen the flexural and tensile modulii of Glass/Phenolic are 10.4 GPa and 13.5 GPa respectively. However with the superior fire performance of phenolic resin, the Glass/Phenolic exhibits very low flammability. In cone test, Glass/Phenolic ignited at 164 s which is much higher than other results, and burned with very low PHRR of 110 kW/m^2

producing 25 MJ/m^2 of THR. Glass/Phenolic also produced low smoke, i.e. 336 L during combustion. Due to low flammability, Glass/Phenolic could achieve V-0 rating in the UL-94 test. Glass reinforced-bio thermoset resin, poly(furfuryl alcohol) composite (Glass/Furan) exhibits relatively low mechanical performance shown by the flexural modulus of 9.0 GPa and tensile modulus of 7.7 GPa, but high fire performance, shown by the high TTI (191 s); low PHRR (174 kW/m^2), THR (17 MJ/m^2) and TSR (22 L) in the cone calorimetric results. In UL-94 Glass/Furan achieved V-0 of vertical rating. These results show that the mechanical and fire performance of Glass/Furan are in similar range to Glass/Phenolic which is due to the similar char forming nature of polyfurfuryl alcohol and phenolic resins. In case of glass reinforced thermoplastic (PP) composites (Glass/PP), their mechanical properties are much lower in comparison to thermoset composites, with flexural modulus of 6.6 GPa and tensile modulus of 9.8 GPa. This is due to the low mechanical properties of PP matrix as compared to thermoset polymer matrices. In term of fire performance, the results show that as expected, Glass/PP is highly flammable in comparison due to the high flammability of PP. The cone calorimetric results tested at 35 kWm^2 indicate that Glass/PP ignited at very shorter time of 25 s, and burned with very high PHRR and THR of 506 kW/m^2 and 80 MJ/m^2 respectively. It must be noted that all thermoset composites were tested at 50 kW/m^2 external heat flux.

Natural fibres have been used as reinforcement in various polymer matrices. The examples of natural fibre composites discussed here are flax reinforced bi-functional epoxy (Flax/EP-L), polypropylene (Flax/PP), and polylactic acid (Flax/PLA). Flax/EP-L composite shows the mechanical properties of 10.0 GPa flexural modulus and 8.8 GPa tensile modulus. The cone calorimetric results of Flax/EP-L tested at 50 kW/m^2 heat flux show high flammability with low TTI of 35 s; high PHRR (616 kW/m^2) and THR (96 MJ/m^2). During combustion, Flax/EP-L produced large amount of smoke (3038 L). Flax/EP-L also failed in UL-94 vertical rating test. The results in Table 1.2 show that Flax/PP exhibits low mechanical properties, 7.4 GPa flexural modulus and 6.4 GPa tensile modulus. The cone calorimetric results at 35 kW/m^2 heat flux show that Flax/PP ignited at 31 s, and burned with 452 kW/m^2 of PHRR producing 98 MJ/m^2 THR and 970 L of TSR. The polylactic acid (PLA) matrix, Flax/PLA, has slightly better mechanical performance than Flax/PP shown by the higher flexural and tensile modulus of 13.7 GPa and 9.0 GPa respectively. Flax/PLA also displayed better fire performance than Flax/PP as can be seen from the cone calorimetric results where Flax/PLA has higher TTI of 34 s; lower PHRR of 313 kW/m^2, THR of 58 MJ/m^2, and TSR of 58 L.

These results show that as compared to the existing carbon/glass fibre reinforced composites, natural fibre composites generally have lower mechanical and fire performance. And on considering the fire regulations of different applications as discussed in *Section 1.3*, the low fire performance of natural fibre composites cannot conform to the majority of the regulations as they are very stringent. Therefore, currently the majority of their applications are mainly in automotive industry due to less stringent fire regulations in this area [9]. Therefore, to expand

the use of natural fibre composites in other applications, flame retardant treatments/modifications are needed in order to improve their fire performances.

1.5 Research aims and objectives

The main aim of this PhD work is to develop flame retardant natural fibre composites for high performance applications by FR treated fibres and/or polymer matrices with FR treatment. To achieve this aim, a number of objectives identified are as:

1) Identify inherently flame retardant materials (natural fibres and biopolymers); FR treatments for natural and melt spun fibres and FR application processes
2) Modify natural fibres and/or natural-thermoplastic comingled/woven textile structures to improve their flammability and fibre-matrix compatibility
3) Develop flame retardant biopolymer fibres/matrices
4) Fabricate a series of composites by using different combinations based on the outcome of (1) – (3), and test for their flammability and mechanical performance
5) By iteration refine outcomes of (4) by both fibre and matrix modifications in order to achieve composites capable of meeting the fire performance requirements for automotive, rail or marine sectors

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Chapter 2: Literature review

Composites are engineering materials composed of two or more components: a matrix and a reinforcing element [1]. In fibre reinforced polymer composites, the reinforcing fibres are embedded in a continuous phase of polymer matrix. The reinforcing fibre provides mechanical strength, while the polymer matrix acts as a binder and provides other good properties such as chemical and electrical properties. In composites, while the mechanical properties are mainly influenced by the mechanical properties of reinforcing fibres, the flammability is influenced by both components. In this chapter, the composition of composites, fire and mechanical properties of constituent components and their derived natural fibre composites are discussed. Various methods of flame retarding individual components and the resulting composites are also reviewed.

2.1 Constituents of natural fibre composites

Similar to other conventional fibre reinforced composites, the natural fibre composites consist of two main components, fibre reinforcement and polymer matrix. A variety of natural fibres and polymer matrices used as components in natural fibre composites are discussed in the following sections.

2.1.1 Natural fibres

Natural fibres can be classified into three main categories based on sources of their origin, namely plant, animal and mineral as shown in Figure 2.1.

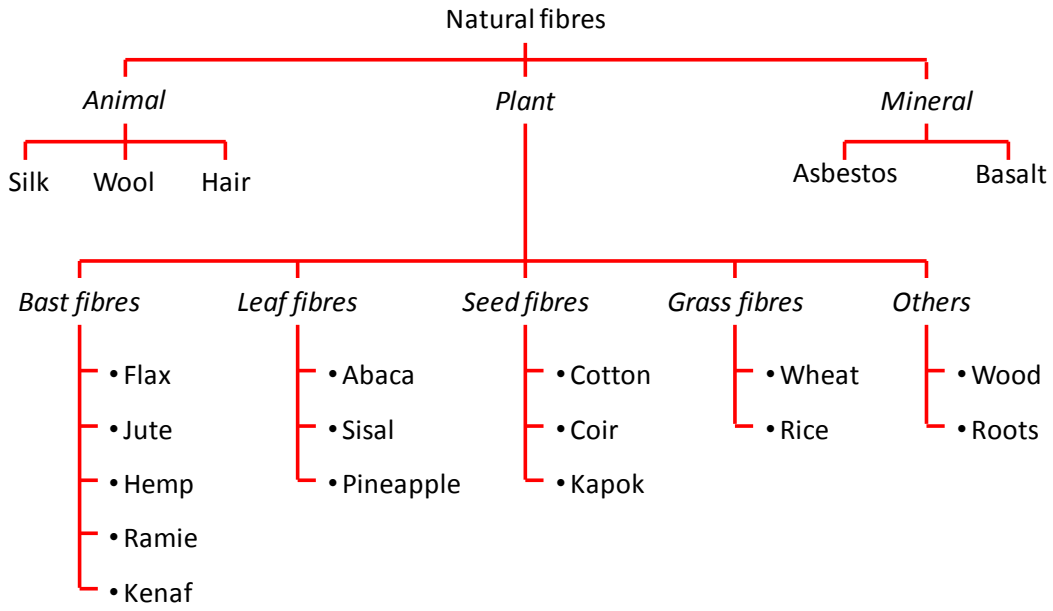

Figure 2.1: Types of natural fibres classified by source of their origin [4,15]

The physical and mechanical properties of these fibres reported in literature are given in Table 2.1. From Table 2.1 it can be seen that the mechanical properties of natural fibres vary, depending on their source of origin. Plant fibres have relatively high mechanical properties and low density providing high strength-to-weight ratio, hence being more favourable and widely used in natural fibre composites [2-14]. Since only plant fibres are relevant to this work, only these are discussed here in details.

Table 2.1: Physical and mechanical properties of natural fibres [3,5,14-18]

Fibres	Diameter (μm)	Density (g/cm^3)	Tensile modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)
Cotton	16-21	1.5-1.6	5.5-12.6	287-597	2.0-10.0
Flax	40-620	1.4-1.5	27-80	345-1035	1.2-3.2
Hemp	16-50	1.4-1.5	3-90	690	1.3-4.7
Jute	30-140	1.3-1.5	3-55	393-773	1.4-3.1
Ramie	40-60	1.5	25-128	400-938	2.0-3.8
Sisal	100-300	1.2-1.5	2-3	511-635	2.0-3.0
Kenaf	14-33	1.2	53	930	1.6
Coir	100-450	1.2-1.5	14-47	131-220	14.0-47.0
Wool	15-45	-	2.3-3.4	120-174	25.0-35.0
Silk	10-25	-	5.8-6.1	210-250	20.0-34.0
Asbestos	-	2.6-3.5	-	1500-4400	-

Plant fibres, also known as cellulosic fibres, consist of highly crystalline cellulose fibrils spirally wound in an amorphous phased matrix comprising of hemicellulose, lignin and pectin. The lignin and pectin work as glue between crystalline cellulose fibrils and hemicellulose to hold the structure of cellulose fibrils as shown in Figure 2.2 [3,5,16,20]. The exact chemical composition of the fibres does vary from one to another depending on types of fibre as can be seen from Table 2.2.

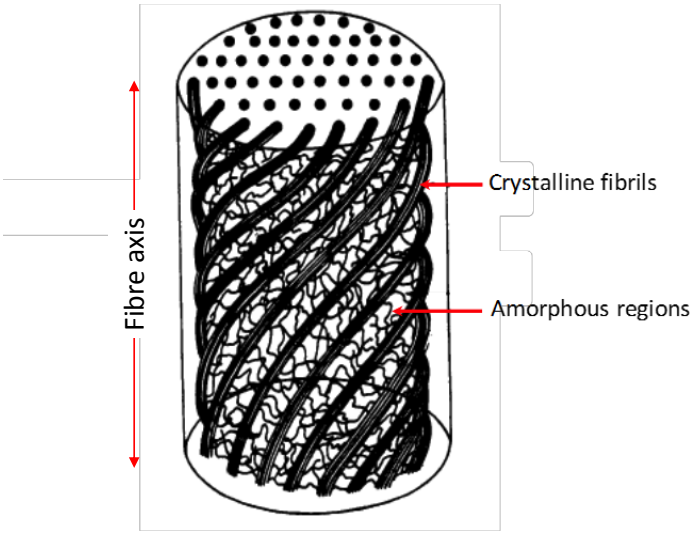

Figure 2.2: Schematic of single fibre cell of cellulosic fibres [3]

Table 2.2: Chemical compositions of plant fibres [5,15,20]

Fibres	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Pectin (%)	Waxes (%)
Cotton	92.0-95.0	5.7	-	1.2	0.6
Flax	62.0-72.0	18.6-20.6	2.0-5.0	2.3	1.5-1.7
Hemp	68.0-74.4	15.0-22.4	3.7-10.0	0.9	0.8
Jute	59.0-71.5	13.6-20.4	11.8-13.0	0.2-0.4	0.5
Ramie	68.6-85.0	13.0-16.7	0.5-0.7	1.9	0.3
Sisal	60.0-78.0	10.0-14.2	8.0-14.0	10.0	2.0
Nettle	53.0-82.6	5.9-12.5	0.5	0.9-4.8	4.0
Kenaf	31.0-72.0	20.3-21.5	8.0-19.0	3.0-5.0	-
Coir	32.0-43.8	0.2-20.0	40.0-45.0	3.0-4.0	-
Pineapple	55.0-68.0	15.0-20.0	8.0-12.0	2.0-4.0	4.0-7.0
Bamboo	26.0-65.0	30	5.0-31.0	-	-

As seen from Table 2.2, the main chemical compositions of cellulosic fibres are cellulose, hemicelluloses, lignin, pectin and waxes. These components have different chemical structures and provide different properties to the fibres.

Cellulose [19]

Cellulose consists of 4000–8000 units of D-glucose ($C_6H_{12}O_6$) monomer linked together to form a long linear polymer chain, Figure 2.3. Cellulose is highly crystalline molecules, and oriented itself into microfibril structure. These microfibrils are attached together through the hydrogen bonds, and form cellulose fibrils. The highly crystalline structure and orientation of polymer chain of cellulose fibrils therefore play an important part in imparting the mechanical properties to cellulosic fibres [3].

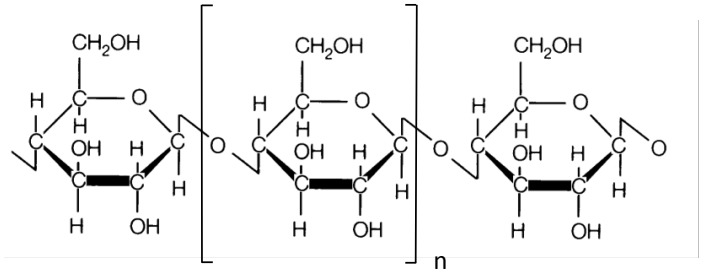

Figure 2.3: Chemical structure of cellulose [11]

Hemicellulose [19]

Hemicellulose is low molecular weight polysaccharide of ten copolymers of glucose, glucuronic acid, mannose, arabinose and xylose. Unlike cellulose that is crystalline structure, hemicellulose is amorphous branched (non-linear structure) of the copolymers having low strength. And they are relatively easy to be hydrolysed in comparison to cellulose.

Lignin [19,21]

Lignin is formed by the non-reversible removal of water molecule from the molecules of sugars, mainly xylose, to form an aromatic structure. There are many types of lignin monomer in the nature depending on sources of sugars in the fibres. In nature, these lignin monomers can also undergo condensation reaction to form larger three dimensional cross-linked molecules. In cellulosic fibres, lignin acts as glue between crystalline cellulose fibrils to hold its structure as shown in Figure 2.2. Hence higher lignin content provides more mechanical stability to the fibres [11]. In addition, due to its aromatic structure lignin also provides high thermal stability and microorganism resistance to the fibres as compared to other components.

Pectin [3]

Pectin is a group of polysaccharides which consist mainly of galacturonic acid. Pectin is normally water resistant, but prone to hydrolysis in alkali solution. In cellulosic fibres, the function of pectin is similar to that of lignin as it works as a bonding agent to hold the structure of crystalline cellulose fibrils in the amorphous phase of hemicelluloses.

Waxes [3,22]

Waxes generally consist of long chain esters of different alcohols which are insoluble in water. In cellulosic fibres, the fibres are covered with waxes on the surfaces providing the protective layer to prevent drying (moisture evaporation) and microbial entry inside the fibres.

In the following section, the mechanical, thermal, and flammability properties of cellulosic fibres with respect to the properties and content of these chemical components are discussed in details.

2.1.1.1 Mechanical properties

The crystalline structure of cellulose fibrils, with higher strength than other chemical components of cellulosic fibres, is the important factor that determines the mechanical properties of the fibres. The difference in mechanical properties of different cellulosic fibres is due to the fact that the content and orientation of crystalline cellulose fibrils vary from fibre to fibre [3,15]. The cellulose content has influence on the properties of cellulosic fibres as in general the fibre with high cellulose content has higher mechanical properties than the low cellulose content fibre. Based on the structure of cellulosic fibre where the cellulose fibrils spirally wound in amorphous matrix of hemicellulose as shown in Figure 2.2, Bledzki et al have explained that the orientation of crystalline cellulosic fibrils with small spiral angle, to the fibre axis, provides higher mechanical strength than a larger spiral angle because the fibril orientation of the small spiral angle is more parallel to the fibre axis which is the loading direction [3,23].

In practice the correlation between the fibre strength, the cellulose content and the spiral angle of cellulose fibrils is not very obvious as shown in Table 2.3. This is due to the defects in the natural fibres which occur during harvesting and production play an important role in the mechanical properties of natural fibres [3,19]. Moreover, due to these defects the mechanical properties of the cellulosic fibres are considerably scattered, in particular tensile strength, as seen from Table 2.3, and hence cause the difficulty in finding the correlation between fibre characteristics and mechanical properties [19].

Table 2.3: Mechanical properties of cellulosic fibres, and characteristics of their crystalline cellulose fibrils [3,4,15,19]

Fibres	Cellulose content (%)	Spiral angle of fibrils to the fibre axis (^{o})	Tensile modulus (GPa)	Tensile strength (MPa)
Flax	71	10	26-27	345-1035
Hemp	78	6.2	30-70	690-1110
Jute	61	8	25-26	393-773
Ramie	83	7.5	24-25	400-938
Sisal	67	20	9-20	511-635

On comparing the actual tensile properties of different cellulosic fibres that have been used for natural fibre composites, hemp fibres show the highest tensile modulus as compared to others, which could be due to the high cellulose content and small spiral angle of fibrils, followed by flax, jute and ramie with the tensile modulus of about 25 GPa. Based on these results, the mechanical properties of the fibres can be ranked as: hemp > flax > ramie > jute > sisal.

2.1.1.2 Thermal stability and flammability

As mentioned above, the main chemical compositions of cellulosic fibres are cellulose, hemicelluloses, and lignin at different percentages depending on fibre type. Each component has different thermal stability, hence different thermal and fire properties are observed in different types of fibres.

Cellulose

Pyrolysis/thermal decomposition of cellulose has been extensively studied by Kandola et al [24]. Cellulose pyrolyses through two types of decomposition reactions depending upon the heating condition as seen in Figure 2.4 [5,24]. At temperatures between 200 - 280^{o}C, cellulose undergoes dehydration and depolymerisation reactions, and produces dehydrocellulose which further decomposes to form char and volatile products. At the higher temperature, i.e. 280 - 340^{o}C, it decomposes to form a liquid intermediate product laevoglucosan which subsequently pyrolyses to produce highly flammable volatiles, and a little charred residue. Hence if the cellulose is heated slowly, the first type of reaction is favoured, which leads to high char formation. On the other hand, higher heating rate or if ignited, the flammability will be higher.

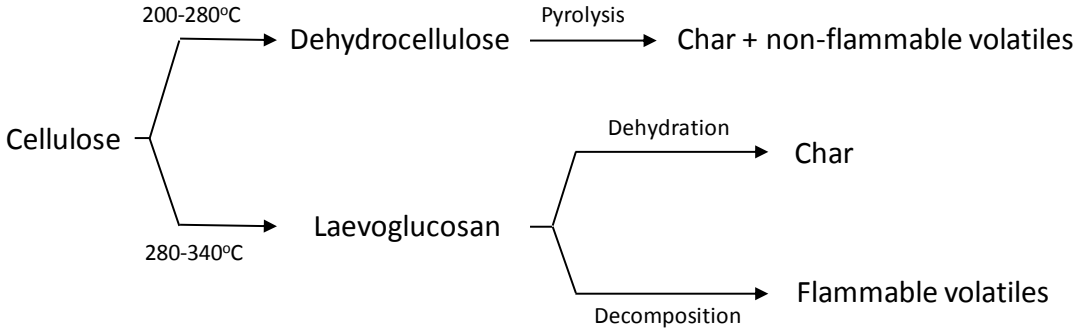

Figure 2.4: Pyrolysis of cellulose [5]

Hemicellulose

The decomposition of hemicellulose mainly undergoes similar reactions as seen in the decomposition of cellulose at low temperatures (200 - 260°C), Figure 2.4, to form dehydrocellulose which subsequently pyrolyses to charred residue and various non-combustible gaseous [5,25]. Hemicellulose is therefore less flammable than cellulose as it decomposes to less flammable products.

Lignin

Lignin which has a three dimensional and highly cross-linked aromatic structure decomposes in the temperature range 160°C to 400°C through two decomposition stages [25,26]. The decomposition at low temperature is related to breaking of the relatively weak bonds between molecules of lignin, whereas at higher temperature the cleavage of bonds in the aromatic rings of lignin monomer takes place. On comparing with decomposition of cellulose and hemicellulose, lignin contributes more to char formation during pyrolysis, which is due to the highly cross-linked aromatic structure of lignin [25].

On analysing thermal behaviour of these three main chemical components of cellulosic fibres, it can be argued that the fibres having higher cellulose content should be more flammable than those containing higher amount of hemicelluloses and lignin. Kozlowski et al have studied the flammability of different cellulosic fibres; hemp, flax, cabuya and abaca fibres by using cone calorimetry [26]. The results showed that flax and hemp, which contain about 2 - 5% lignin content, show lower peak heat release rate and mass loss rate than cabuya and abaca fibres which have higher lignin content of 7 - 13%. The importance of lignin content in the cellulosic fibres has been also studied by Manfredi et al [27]. They compared the thermal stability of flax, sisal and jute by thermogravimetric analysis (TGA). The results are graphically presented in Figure 2.5.

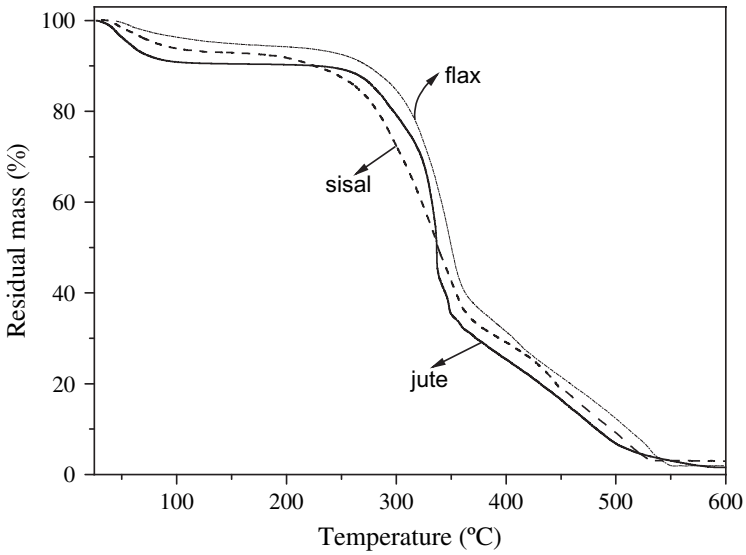

Figure 2.5: Mass loss curves of flax, sisal and jute fibres as a function of temperature in TGA experiment [27]

The content of lignin in flax, sisal, and jute was 2.0, 9.9 and 11.8%, respectively. The results showed that flax with lowest lignin content has higher decomposition temperature than other fibres, but had lower oxidation resistance. These properties are provided by the aromatic structure of lignin, as can be seen from its lower char residue. From these discussions, it can be inferred that the fibres having high lignin content, although are less flammable, have lower onset of decomposition temperatures, which will have an impact on the use of these fibres in composite applications. The onset temperature of fibre degradation is an important criterion when selecting fibre type for use in thermoplastic composites.

2.1.2 Polymer matrices

From the discussion in the above section, it can be clearly seen that the fibres generally start degrading above 180 - 200^{o}C depending on the fibre type, and hence this has limited the choice of polymer for use in natural fibre composites to those which have a processing temperature lower than 200^{o}C in order to avoid the onset of degradation of natural fibres during the laminate preparation. In this section, a number of polymers from two groups, thermoplastic and thermoset, for use as polymer matrix in natural fibre composites are discussed.

2.1.2.1 Thermoplastic polymers

Thermoplastic polymers are processed by melt-moulding techniques, e.g. injection, extrusion, and compression moulding. Hence the suitable thermoplastic polymers for natural fibre composites are selected from those having melting temperature lower than 200^{o}C. The examples of these thermoplastic polymers with their melting temperature and chemical structure are given in Table 2.4 and Figure 2.6 respectively. Among these polymers, polypropylene (PP) is more popular than others for natural fibre composites as can be seen from Table 1.1 (*Chapter 1*). In automotive

applications polypropylene reinforced with different cellulosic fibres are widely used for interior parts and non-load bearing structures [2,5,21,25].

Table 2.4: Thermal characteristics of thermoplastic polymers suitable for natural fibre composites [28 - 31]

Polymers	Glass transition temperature (^{o}C)	Melting temperature (^{o}C)
Polypropylene (PP)	-15	160-220
Polystyrene (PS)	100	177-277
Polymethyl methacrylate (PMMA)	105	160-220
Polyvinyl chloride (PVC)	85	177-212

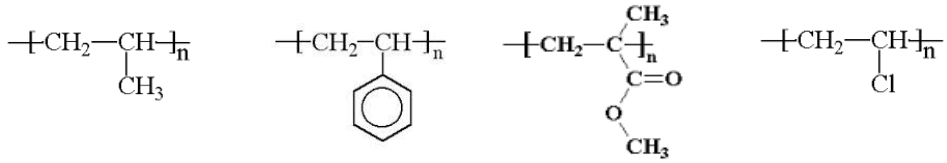

Figure 2.6: Chemical structure of thermoplastic polymers suitable for natural fibre composites

The potential thermoplastic polymer matrices listed above are petroleum based (synthetic) polymers, thereby the natural fibre composites made from these polymers are only partially bio-derived product. Since, the environmentally friendly properties is one of the main advantages of natural fibre composites in comparison to conventional fibre reinforced composites, biopolymers can be used as an alternative choice of a material type for polymer matrix to achieve fully bio derived composites.

Biopolymers are polymers derived from renewable sources such as corn starch and sugar [23,32,33]. The examples of biopolymers are polylactic acid (PLA), polycaprolactone (PCL), polyhydroxyalkonate (PHA), poly-3-hydroxy butyrate-co-valerate (PHBV). Nowadays biopolymers are widely used in many applications such as packaging, fibres, implants and composites [11,33]. In composite applications, polylactic acid (PLA) is commonly used as polymer matrix, especially for natural fibre reinforced composites [5,33,34]. PLA is linear aliphatic polyester derived from crops [35]. Farrington et al explain the manufacturing process of PLA; the lactic acid, which is monomer of PLA, is produced by converting the starch from crops into fermentable sugars (i.e. glucose) by enzymatic hydrolysis reaction, followed by the fermentation of this sugar to form lactic acid, as shown in Figure 2.7 [35]. The lactic acid monomers are then polymerised to polylactic acid by either condensation or ring opening reactions as shown in Figure 2.8 [35,36].

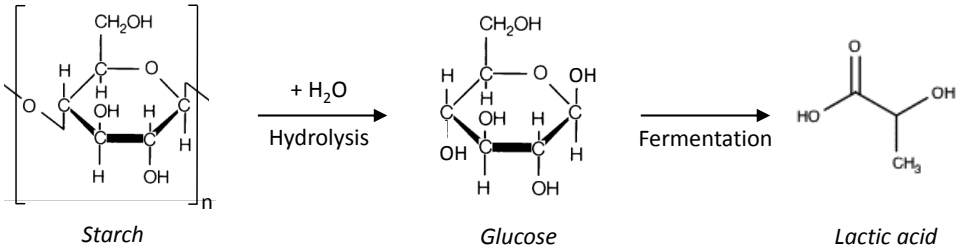

Figure 2.7: Production of lactic acid [35]

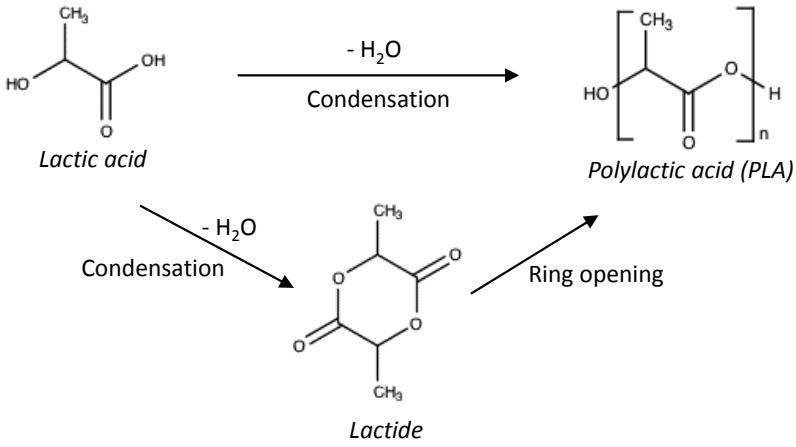

Figure 2.8: Polymerisation of polylactic acid (PLA) [35]

Polylactic acid (PLA) has melting temperature of 160 - 180^{o}C [35,36] which is similar to that of PP, therefore it can be used for polymer matrix of natural fibre composites without causing degradation of natural fibres.

The mechanical and fire properties of the potential thermoplastic polymer matrices are summarised in Table 2.5, which include tensile strength and flexural modulus for mechanical properties, and limiting oxygen index (LOI) and peak of heat release rate (PHRR) for flammability.

Table 2.5: Mechanical properties [31,33,37-41] and flammability [42-45] of selected thermoplastic polymers

Polymers	Tensile modulus (GPa)	Flexural modulus (GPa)	LOI (%)	PHRR (kW/m^2)
Polypropylene (PP)	1.4	2.0	17	1500
Polystyrene (PS)	3.2	3.0	17-18	1100
Polymethyl methacrylate (PMMA)	3.3	3.0	17-18	670
Polyvinyl chloride (PVC)	2.6	3.0	27-45	170-180
Polylactic acid (PLA)	2.6	3.0-3.1	20	680
poly-3-hydroxy butyrate-co-valerate (PHBV)	1.5	1.1	-	-

Note: PHRR results of PE, PP, PS, PMMA and PVC were measured by using cone calorimetry at 40 kW/m^2 heat flux [45], while PLA and PHBV were at 35 kW/m^2 heat flux.

The mechanical properties of selected synthetic thermoplastic polymers taken from literature are reported in Table 2.5. In principle, mechanical properties of thermoplastic polymers are related to many parameters such as glass transition temperature, molecular weight, length of repeating unit, etc. Among these, glass transition temperature, which is one of characteristic properties of polymer, is a simple factor to indicate the difference in mechanical properties of different polymers [31]. Glass transition temperature (T_g) by definition is expressed as the temperature when a phase transition of a polymer, from solid to rubbery, takes place. Hence, at room temperature a polymer with higher glass transition temperature should be more rigid and stiffer than the one with lower temperature [31]. From Table 2.5, the mechanical properties of different polymers show that polymethyl methacrylate, having T_g of 105^{o}C, shows the highest tensile modulus of 3.3 GPa, followed by polystyrene (T_g = 100^{o}C, tensile modulus = 3.2 GPa), polyvinyl chloride (T_g = 85^{o}C, tensile modulus = 2.6 GPa), and polypropylene (T_g = -15^{o}C, tensile modulus = 1.4 GPa). A similar trend is observed for the flexural modulus of these synthetic thermoplastics. For biopolymers, polylactic acid (PLA) with the T_g of 65 - 70^{o}C has similar mechanical properties as PVC with the tensile modulus of 2.6 GPa and flexural modulus of 3.0 - 3.1 GPa, whereas poly-3-hydroxybutarate-co-velarate (PHBV), having T_g of -9^{o}C, shows lower mechanical properties in both tensile and flexural modes as compared to PLA, Table 2.5.

For flammability of these thermoplastic polymers, the limiting oxygen index (LOI), which expresses the minimum percentage of oxygen required to sustain the candle-like burning behaviour of materials [46], shows that most synthetic thermoplastic polymers are highly flammable with low LOI values of 17 - 18%, except polyvinyl chloride (PVC) with a relatively high LOI of 27 - 45%, Table 2.5. This observation is also supported by the cone calorimetric results reported by Hirschler et al. Plaques of PP, PS, PMMA and PVC were horizontally exposed to 40 kW/m^2 external heat flux with the application of a spark ignition as detailed in ISO 5660 [47]. The results in term of peak of heat release rate (PHRR) are given in Table 2.5. Results show that PVC is least flammable of the thermoplastics with PHRR of 170 - 180 kW/m^2, followed by PMMA (670 kW/m^2), PS (1100 kW/m^2), and PP (1500 kW/m^2) respectively. The difference in flammability of these polymers can be explained by the difference in their chemical structures as shown in Figure 2.6. PVC contains chlorine in its structure, and hence during combustion PVC releases HCl gas which can work as a free radical scavenger to interfere with its combustion process. PVC is therefore less flammable than others. On the other hand, PP and PS contain only carbon and hydrogen in their structure, and hence only decompose to small hydrocarbon molecules which are highly flammable, and burn with high PHRR. The PMMA, besides carbon and hydrogen, also contains oxygen in its structure, and hence burns with less flammable products producing lower PHRR as compared to PP and PS. Hence, PVC provides better fire performance in natural fibre composites due to its inherently flame retardant characteristic in comparison to others. However, PVC releases HCl gas during combustion, and hence environmental issues need to be addressed when using PVC in natural fibre composites. For biopolymers, only the flammability results of PLA are available in literature. PLA has been reported to be having relatively lower flammability as compared to most of synthetic polymers,

in particular polyolefins [5,35]. It can be seen from Table 2.5, PLA has higher LOI (20%) and lower PHRR (680 kW/m^2) as compared to other synthetic polymers, except PVC. Similar trends were observed from the cone calorimetric results of PP and PLA plaques tested by Kandola et al at 35 kW/m^2 external heat flux [44]. They reported PLA shows less flammability with lower PHRR (663 kW/m^2) and total heat released (THR, 50 MJ/m^2), as compared to 1700 kW/m^2 PHRR and 95 MJ/m^2 THR of PP. This is due to the chemical structure of PLA which contains oxygen atoms in its structure, and hence it tends to burn with more char formation and less flammable product, as compared to PP which decomposes with highly flammable product of small hydrocarbon molecules as it contains only carbon and hydrogen.

2.1.2.2 Thermoset polymers

Thermoset resins are well known polymer matrices that have been used widely in composites, especially glass reinforced composites, for many applications. The selection of thermoset resins for natural fibre composites is also based on the processing technique of the resins. Unlike thermoplastics, thermoset resins are processed by curing the mixture of monomer or pre-polymer and catalyst or crosslinking agent through the irreversible chemical reaction at desired temperature in order to form the crosslinking network between polymer chains of the resin. The examples of thermoset resin matrices that require a curing temperature lower than the onset of decomposition of natural fibres are unsaturated polyester, vinyl ester, and low temperature curing epoxy. It has been reported in literature these resins and resole type of phenolic resins are used as polymer matrices in composites reinforced with natural fibres including flax, jute, sisal, abaca, kenaf, pineapple and coir [2,5,7,15]. Similar to thermoplastic natural fibre composites, to obtain better advantage on environmental friendly aspect bio based thermoset resin is an alternative material. Currently a number of bio-based thermoset resins on the market, most of which are polyester resins derived from plant oil such as soybean and castor oils [48]. These resins however still need synthetic chemical crosslinking agents (i.e. isocyanates, amines) to cast the resins to solid polymers, and hence they are in fact only partially bio-based materials. Alternatively, to achieve fully bio based composites, poly(furfuryl alcohol) (PFA), also known as furan resin, is of interest as it is a fully bio based thermoset resin derived from sugarcane bagasse [4,49-54]. The manufacturing process of polyfurfuryl alcohol starts from the production of furfuryl alcohol by the dehydrogenation of furfural which is obtained from the hydrolysis reaction of hemicellulose in bagasse, Figure 2.9 [51,53-55].

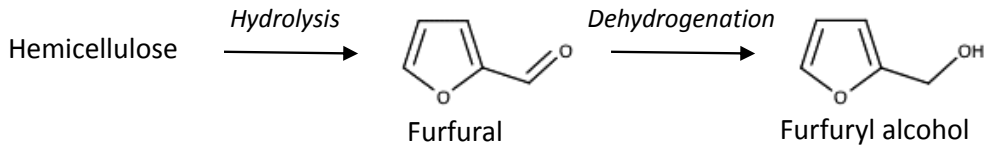

Figure 2.9: Production of furfuryl alcohol from hemicellulose in sugarcane bagasse [55]

The furfuryl alcohol undergoes self-polymerisation to form highly crosslinked network of poly(furfuryl alcohol) at the evaluated temperature under acidic condition (i.e. addition of acetic acid or sulphuric acid) through the condensation polymerisation and crosslinking reaction as shown in Figure 2.10 [53-55].

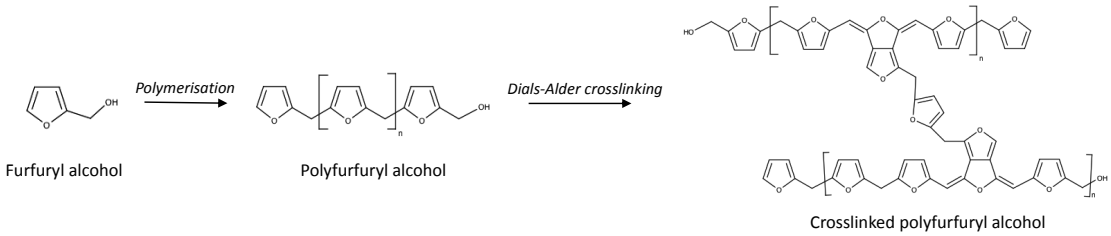

Figure 2.10: Polymerisation and crosslinking reactions of poly(furfuryl alcohol) [53]

The typical mechanical and fire properties of synthetic and bio based thermoset resins, discussed above, are given in Table 2.6. The tensile modulus of synthetic thermoset resins show that low temperature curing epoxy (EP) and vinyl ester (VE) are higher than others, followed by unsaturated polyester (UP) and resole phenolic (PH) respectively. On comparing the flexural properties of these synthetic thermoset resins, UP, VE and EP have similar performance as shown by the flexural modulus of 3.0 - 3.9 GPa, whereas the flexural modulus of PH is lower (2.0 - 2.5 GPa). Based on the properties in both tensile and flexural modes, EP and VE are the strongest synthetic thermoset polymer matrix for producing natural fibre composites, whereas PH is the weakest one. The bio based resin, poly(furfuryl alcohol) has lower mechanical performance in comparison to most of synthetic thermoset resins. The reported tensile modulus of poly(furfuryl alcohol) is 2.8 GPa, while the flexural modulus is 2.8 - 2.9 GPa.

Table 2.6: Mechanical properties [56-62] and flammability [43] of selected thermoset resins

Polymers	Tensile modulus (GPa)	Flexural modulus (GPa)	LOI (%)
Unsaturated polyester (UP)	3.1	3.5-3.9	20-22
Vinyl ester (VE)	3.3	3.1-3.2	20-23
General purpose epoxy (EP)*	3.3	3.0-3.8	22-25
Resole type Phenolic (PH)	2.5	2.0-2.5	25-33
Polyfurfuryl alcohol (PFA, Furan)	2.8	2.8-2.9	35-40

Note: The properties of epoxy resin reported in the table are of general purpose grade, which is low temperature curing type.

Regarding flammability, the comparison of LOI values for the synthetic resins reported in Table 2.6, can be ranked for fire performance as shown below:

Phenolic > epoxy > unsaturated polyester ~ vinyl ester

Phenolic shows superior fire performance in comparison to the other resins. This is due to the cross-linked aromatic structure of phenols, which has high thermal stability, and hence exhibits

higher fire performance. The flammability ranking of these synthetic resins can only be used in generic terms. It can be seen from Table 2.6 that the LOI values of some resins are reported as a wide range, i.e. epoxy and phenolic resins. The LOI value of epoxy is reported in the range of about 22 - 25%. This is because the functionality of the resin affects the flammability of thermoset resins [5]. Katsoulis et al compared the flammability of different types of epoxy resins by using LOI [63]. The results show that the LOI of epoxy with higher functionality (tetra-functional) is 27.8%, whereas the one with low functionality (bi-functional) has LOI of 21.5%. This shows that the epoxy resin with low functionality is more flammable than the high functionality resin. For polyfurfuryl alcohol, the result shows it has low flammability similar to that of phenolic resin with LOI of 35 – 40%, related to the high crosslinked aromatic structure of polyfurfuryl alcohol, similar to that of phenolic resin [54,62,64-66].

2.2 Fabrication techniques for natural fibre composites

A number of processing techniques are available for natural fibre composite fabrication. These are divided into two main categories based on types of polymer matrix, i.e. thermoplastic and thermoset polymers.

2.2.1 Thermoplastic natural fibre composites

Thermoplastic natural fibre composites can be prepared from natural fibres of various forms, such as short fibres, long fibres, and textile fabric structures by using different fabrication techniques. The examples of commonly used techniques are discussed here.

2.2.1.1 Compounding

Melt compounding is one of the common techniques used for introducing additives or fillers into thermoplastic polymers by using a twin-screw extruder. Short fibre-reinforced composites are prepared by compounding. Compounding uses mechanical shear energy to have a homogeneous dispersion of natural fibres in the polymer matrix. In the compounding process, natural fibres and polymer pellets are fed through the heated barrel of a twin-screw extruder to melt the polymer. The screws are rotated at relatively high speed to convey the mixture of molten polymer and natural fibres along the barrel from feeder to nozzle zones; developing shear stress in the mixture to obtain a good dispersion of natural fibres in the polymer matrix. Strands of the molten polymer with natural fibres emerges from the nozzle of the extruder and are then pulled through the water bath to cool, followed by pelletising the strand by using a rotary grinder. The compounded fibre/polymer pellets are then moulded into required shape by injection or compression moulding. In injection process, fibre/polymer pellets are fed in a heated barrel of injection machine to melt the polymer matrix, and then injecting the molten phase of fibre/polymer into a mould. To process by compression moulding, the fibre/polymer pellets are place in a mould of desired shape, and heated to a temperature required to melt the polymer

matrix under pressure by using a hot press, and then cooling down to ambient temperature under pressure.

2.2.1.2 Film Stacking

Film stacking is a technique that allows natural fibre composites to be fabricated from short fibres, long fibres, or fabric structures. In this technique, the fibres or fabrics are placed between layers of thermoplastic polymer films. The assembly is then heated in a mould to the temperature required to melt the polymers by using a hot press. Pressure is applied on the assembly while heating to force the molten polymer to flow and impregnate the natural fibres. The processing conditions, such as temperature, pressure, and dwelling time need to be controlled as these parameters have significant impact on the properties of the produced composites. The temperature and dwelling time should be only sufficient to melt the polymer matrix without causing thermal degradation of natural fibres. The pressure applied on the assembly also needs to be adjusted at an appropriate level as the low pressure could cause high void content and un-wetted fibres in composites, while de-alignment of reinforcing fibres would occur when the pressure is too high.

2.2.1.3 Consolidation of thermoplastic composite preforms

In this technique, the fabrication of thermoplastic natural fibre composites is divided in two stages. These include preparation of the composite preforms/prepregs, and consolidation process which is usually done by using melt-pressing similar to that discussed in the film stacking technique. Therefore, the discussion in this section is mainly focused on the preparation of the composite preforms. The preforms of thermoplastic natural fibre composites are generally in textile structures as most of them are prepared by using textile manufacturing processes [67-70].

Anand et al have developed a patented manufacturing process for nonwoven thermoplastic composite preforms by using textile needle punching [68]. Two layers of (a) nonwoven web of polymer fibres and (b) woven fabric of natural fibres are fed through a needle punching machine to physically bind them together, and form a preform of thermoplastic natural fibre composites, Figure 2.11 [44,68].

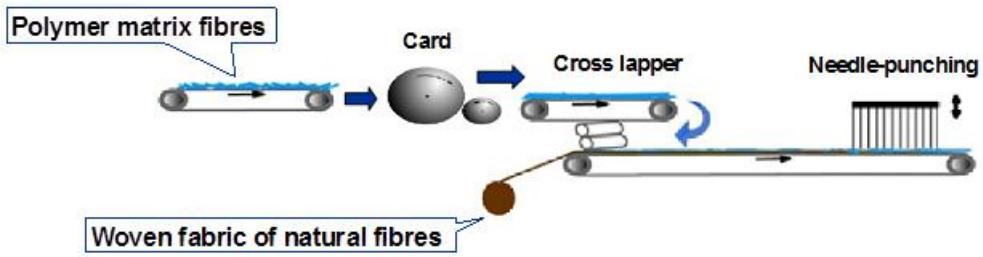

Figure 2.11: Manufacturing process of nonwoven thermoplastic natural fibre composite preforms

Another example of textile processing used for preparing preforms of thermoplastic natural fibre composites is commingling [69-71]. In this technique, natural fibres and thermoplastic fibres are blended intimately at the filament level, and then processed to natural fibres/polymer commingled yarns. This leads to uniform distribution of natural fibres in the polymer matrix system of composites in comparison to composites prepared by other techniques [71]. The commingled yarns can be produced in several ways. In general, the natural and thermoplastic fibres are spread out on top of each other, and blended together by using different textile processing techniques such as carding, blowing air, blading, core-spinning, etc. [71-72]. These commingled yarns are then used to make fabric preforms by weaving and knitting [71].

2.2.2 Thermoset natural fibre composites

Thermoset natural fibre composites can be fabricated in several ways by using manufacturing processes available for conventional fibre reinforced thermoset composites [70]. The details of these processes are described below.

2.2.2.1 Vacuum bagging

Vacuum bag moulding is a common manufacturing technique that is widely used in aerospace and marine applications [57,73]. The advantages of this technique over others are the ability to form complicated shape and high fibre volume fraction composites. In this manufacturing process, the mixture of liquid resin and its catalyst/hardener is applied to a mould, and then the natural fibres reinforcement is placed on top of the layer of resin. A roller is used to impregnate the fibres with resin as well as to remove entrapped air. The process is repeated until a desired thickness is obtained. The mould containing resin and natural fibre reinforcement is then vacuum bagged, and heated in an oven to the required temperature for curing the resin.

2.2.2.2 Resin transfer moulding

Resin transfer moulding (RTM), also known as a liquid transfer process, is another of the commonly used methods by industry for thermoset composite fabrication [57]. With this technique, composites are usually fabricated from fibre reinforcement in fabric form. Layers of reinforcing fabrics are placed in cavity of a mould to obtain a desired thickness, and then the mixture of liquid resin and its catalysts/hardeners is pumped into the mould until its cavity is completely filled through single and multiple inlet ports in the mould [73]. The entire mould is then heated to the curing temperature for a period of time, dependent on the kinetics of the resin mixture and thickness of the composite. The key parameters of the RTM process are viscosity of resin and permeability of the reinforcing fabric as these affect the resin impregnation of the fibres. High viscosity of resin and low permeability of fabrics can cause difficulty in flow of resin during the mould filling stage of RTM, leading to incomplete impregnation of reinforcing

fibres. Therefore, low viscosity resin and high permeability reinforcing fabrics are favoured for this technique.

2.2.2.3 Pultrusion

Pultrusion is a continuous moulding process for producing long structural composites, such as solid rods, hollow tubes, flat sheets and beams, with constant cross section. In the pultrusion process, continuous fibre bundles are pulled through a resin bath, followed by passing through a long pre-heated die, Figure 2.12.

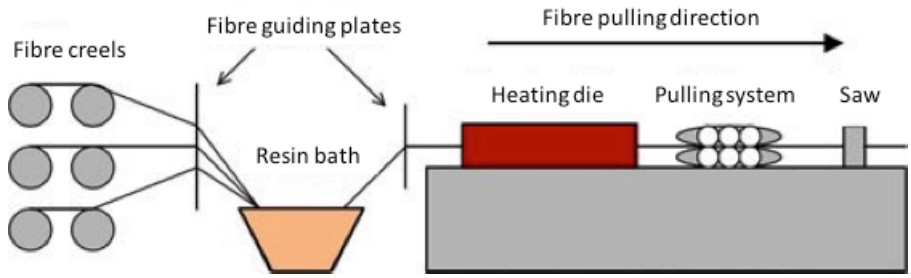

Figure 2.12: Illustration of pultrusion process [74]

The important parameters for controlling the quality of composites prepared by using pultrusion are the viscosity of resin and the pulling speed of fibres as these play an important role in the properties of the impregnated fibres [57]. In general, low viscosity resin and a slow fibre pulling speed provide better resin penetration of impregnated fibres, while the high viscosity resin and fast fibre pulling speed improve the amount of resin pick up of the fibres owing to increased drag force [75].

2.2.2.4 Consolidation of thermoset natural fibre composite preforms/prepregs

The preform of fibre reinforced thermoset composites, also known as prepreg, is fabricated by using the process similar to that of pad-dry technique used in textile applications. The continuous yarns or fabrics of fibre reinforcements are passed through a resin bath to impregnate the fibre, followed by passing through rollers, where pressure is applied, to squeeze out the excess resin. The percent resin pickup of the impregnated yarns/fabrics can be controlled by adjusting the pressure applied on the rollers as lower pressure allows a higher amount of resin to be picked up. After impregnation, the rein-impregnated yarns/fabrics are partially cured by using a continuous dryer to form prepregs. To prepare composites from these prepregs, different manufacturing techniques can be used such as vacuum bagging and compression moulding. For vacuum bagging, similar process as described in *Section 2.2.2.1* can be used with a slight difference that instead of applying resin and fibre reinforcement manually, layers of prepregs are placed in a mould, followed by vacuum bagging and heating the mould in an oven. While in the compression moulding process, the layers of prepregs are placed on a mould in a desired fibre orientation, and then heated to the temperature required for curing the resin under pressure by using a hot press machine.

2.3 Performances of natural fibre composites

2.3.1 Mechanical performance

The mechanical properties of composites depend upon the properties of fibre reinforcement and polymer matrix, and the interaction between them [1]. Bledzki et al have studied the effect of polymer matrix on the mechanical performance of natural fibre composites by comparing the properties of jute fibre reinforced composites prepared with different polymer matrices including polypropylene (PP), poly-3-hydroxybutarate-co-velarate (PHBV), and polylactic acid (PLA) [76]. The short fibre reinforced composites were prepared with 30 wt-% of fibre content by using a twin-screw extruder, and then moulded to test specimens by using an injection moulding machine. The tensile properties of these composites and the respective polymer matrices are given in Table 2.7.

Table 2.7: Tensile properties PP, PHBV and PLA polymers, and its composites reinforced with jute fibres at 30 wt-% fibre content [77]

Matrix	Reinforcing fibres	Tensile modulus (GPa)	Tensile strength (MPa)
PP	-	1.5	29
	Jute	5.8	48
PHBV	-	2.1	27
	Jute	7.0	35
PLA	-	3.4	64
	Jute	9.6	82

The results in Table 2.7 show that among different polymers, PLA has highest tensile modulus and strength. Jute fibre reinforced PLA composite also shows the highest tensile performance, followed by jute fibre reinforced PHBV and then PP. This shows that polymer matrix can affect properties of composites. The effect of different types of reinforcing fibres on mechanical performance of natural fibre composites has been studied by Kandola et al who have compared the tensile properties of PP reinforced with woven fabrics of different natural fibres including sisal, jute, and wool [44]. The preforms of natural fibres/polypropylene (40/60 by weight) were prepared by physically bonding the nonwoven mat of polypropylene fibres and woven fabrics of natural fibres together by using needle punching. The eight layered composite laminates from each type of these preforms were then produced by using melt pressing, and tested for their tensile properties. The tensile properties of these composites are given in Table 2.8.

Table 2.8: Tensile properties of PP composites reinforced with sisal, jute and wool fibres [44]

Matrix	Reinforcing fibres and its tenacity at break	Tensile modulus (GPa)	Tensile strength (MPa)
PP	-	2.7	24
	Sisal, 0.13N/Tex	4.9	40
	Jute, 0.04N/Tex	3.7	35
	Wool, 0.02N/Tex	1.4	29

The tensile properties in Table 2.8 show that the PP composites reinforced with sisal, the strongest fibres (0.13 N/Tex tenacity) in comparison, exhibit higher tensile performance than the others, followed by PP composites reinforced with jute and wool fibres respectively. Moreover, the tensile properties of PP composite reinforced with wool, which is a weak fibre (0.02 N/Tex tenacity), show that the tensile properties of the composites are even lower than that of pure PP sample. From these studies, it can be concluded that to obtain high mechanical performance natural fibre composites, both reinforcing fibres and polymer matrix with high mechanical properties are required.

Besides the properties of composites' components, the interaction between fibres and polymer matrix phases, also called fibre/matrix interfacial adhesion, which is related to the efficiency of stress transfer from the polymer matrix to reinforcing fibres in composite system, also plays an important role on the mechanical properties of composites, in particular tensile properties [3,15]. The higher fibre/matrix interfacial adhesion gives better load-transfer between fibre reinforcement and polymer matrix, so results in higher mechanical performance of composites. With the use of natural fibre in composites, the interfacial adhesion between natural fibres and polymer matrix, especially hydrophobic polymer such as polyethylene (PE) and polypropylene (PP), is one of the major problems. This is due to the incorporation of hydrophilic natural fibres into polymer matrix, which is relatively of hydrophobic character usually cause lack of adhesion between fibre and matrix, and hence leading to the inefficient stress transfer from polymer matrix to reinforcing fibres, resulting in lower mechanical properties than expected of natural fibre composites [3,15]. In order to achieve the high fibre/matrix interfacial adhesion surface modification of natural fibres is required [3,15,77-81]. Commonly used surface treatments include alkali and silane treatments. The details of these potential surface modification treatments are discussed in details in *Section 2.4.1*.

2.3.2 Fire performance

Fire performance of natural fibre composites is a major concern due to the fact that both reinforcing and polymer components of natural fibre composites are combustible, unlike other conventional composites such as glass and carbon fibre reinforced composites where only polymer matrix is flammable. Although there is a vast range of literature about the usage of natural fibres as reinforcement in composites, there is a limited published literature available on the flammability study of these composites. This could be because their main application is in automotive industry, where the fire regulation is not stringent [5]. The flammability of natural fibre composites reported in literature is studied mainly for academic purposes where cone calorimetry has been used [5,25,26,82-86].

In general, the presence of fibres reduces the flammability of polymer. To show this effect, Le Bras et al have studied the flammability of flax fibre-reinforced polypropylene composites and compared with neat polypropylene by using cone calorimetry at 50 kW/m^2 external heat flux

[82]. The composites were prepared by compounding short fibres of flax with PP matrix by using a twin-screw extruder at 40 wt-% fibre content, and then pressed to 3 mm thick plaques using a hot press. The presence of flax fibres in the composites reduced the time-to-ignition (TTI) of neat polypropylene (PP) from 45 s to 30 s, and peak of heat release rate (PHRR) from 1800 kW/m^{2}of neat polypropylene to 640 kW/m^2. Moreover, the composites burned for longer time than neat polymer. This shows that fibres reduced TTI and propensity of burning, i.e. they burned slowly but for a longer time. Schartel et al also studied the flammability of 5 mm thick laminates of flax reinforced PP composite (30/70 by weight) by using cone calorimetry at 50 kW/m^2 [84]. They reported that besides the longer burning time, the thick laminates (5mm thickness) of flax fibre reinforced PP composite also burned with two peaks of HRR in cone calorimetry rather than single peak as observed in neat polymer. They explained that the first peak represents the burning of flax reinforced PP laminate after ignition. During this stage the flax fibres on the surface start charring to form carbonaceous layer which could act as thermal barrier for the underlying materials to slow its burning. Once this charred layer cracks, the second peak of HRR then appears due to the increase in rate of combustion of underlying materials after the rupture of the protective layer. The fibre content in a composite also affects the flammability of composites. Helwig et al have compared the flammability of flax reinforced PP composites containing different percent fibre content [83]. The composites were prepared from long flax fibres (150 - 300 mm long) where the fibres were placed between layers of PP sheets, and then melt-pressed to 5 mm thick laminates at 12.5, 20, 30 and 40 wt-% fibre content. The flammability of the laminates was measured by using a cone calorimeter at 35 kW/m^2. The results reported in Table 2.9 show that the composites with higher flax content show greater reduction in TTI, PHRR, and effective heat of combustion (EHC) as compared to that of composites with lower flax content.

Table 2.9: Cone calorimetric results of flax reinforced PP composites tested at 35 kW/m^2 [83]

Fibre cont. in composites (wt-%)	TTI (s)	1st PHRR (kW/m^2)	2nd PHRR (kW/m^2)	EHC (MJ/kg)
0	62	1200	-	41.6
12.5	45	480	750	39.2
20.0	45	470	560	37.2
30.0	39	440	380	34.2
40.0	35	290	380	33.1

Table 2.10: Cone calorimetric results of natural fibre reinforced unsaturated polyester and acrylic composites at 35 kW/m^2 [27]

Polymer matrix	Reinforcement	TTI (s)	THR (MJ/m^2)
Acrylic	Flax	110	105
	Sisal	52	101
	Jute	72	74
Unsaturated polyester	Jute	51	78

Manfredi et al have studied the effect of polymer matrix and type of natural fibre on the flammability of composites by using cone calorimetry at 35 kW/m^2 heat flux [27]. The 4 mm thickness laminates of acrylic and unsaturated polyester reinforced with fabrics of different natural fibres, including woven jute fabric, nonwoven flax and sisal fabrics, were prepared by using vacuum infusion technique. The fibre content was 30% by volume in all samples. The cone calorimetric results of these composites are given in Table 2.10. On comparing the effect of polymer matrix, the cone calorimetric results of jute reinforced acrylic and unsaturated polyester showed that the jute reinforced unsaturated polyester (Jute/UP) was slightly more flammable than jute reinforced acrylic composites (Jute/Acrylic) as can be seen that the Jute/UP ignited at 51 s and burned with total heat released (THR) of 78 MJ/m^2, while Jute/Acrylic showed 72 s and 74 MJ/m^2 of TTI and THR respectively. Different types of natural fibre reinforcement showed variable effects on fire performance in natural fibre acrylic composites which could be due to the different thermal and fire properties of each fibre type. The results in Table 2.10 show that acrylic reinforced with flax has the longest TTI of 110 s, followed by jute and sisal respectively. The THR results show that acrylic reinforced with flax and sisal burned with similar THR of 100 - 105 MJ/m^2, whereas jute reinforced composites burned with lower THR of 74 MJ/m^2. Similar observations have been reported by Kandola et al [44]. They have compared the flammability of polylactic acid (PLA) and polypropylene (PP) composites reinforced with jute, sisal and wool fibres. The reinforcement used in this work was woven fabric with variable area densities dependent on type of fibres: jute (area density: 174 g/m^2), sisal (fabric area density: 62 g/m^2) and wool (area density: 171 g/m^2). The composite preforms with 40 wt-% fibre content were made by needle-punching a layer of each type of woven fabric with a nonwoven mat of PP or PLA. An assembly of 8 layers of each preforms was then melt-pressed to laminates, and tested for their flammability by using cone calorimetry at 35 kW/m^2. The results are given in Table 2.11.

Table 2.11: Cone calorimetric results of natural fibre reinforced PLA and PP composites at 35 kW/m^2 [44]

Sample	Thickness (mm)	TTI (s)	PHRR (kW/m^2)	THR (MJ/m^2)	TSR (litre)	Yield (%)
PLA	2.5	28	663	50	0.7	3.0
Jute/PLA	3.0	38	393	61	0.9	4.4
Sisal/PLA	1.3	27	542	28	1.2	3.3
PP	2.7	30	1699	95	1300	0.0
Jute/PP	3.2	33	675	96	1120	3.3
Sisal/PP	1.3	25	680	43	530	3.2
Wool/PP	3.6	30	632	140	1930	4.6

On comparing PP neat polymer and its derived natural fibre composites, the results show that the addition of all natural fibres shows small effect on TTI, but reduced PHRR of PP by about 60 - 70%. Among these fibres, wool fibre exhibits the highest reduction followed by jute and sisal. This is as expected from the flammability of these fibres (see *Section 2.1.1.2*). However, the total heat release (THR) of all composite samples is higher than neat PP polymer, except sisal

reinforced PP composite as its thickness is lower than other samples Table 2.11. In general, thickness affects the flammability of sample as a thin sample ignites early, burns for shorter time, and produces less total heat release than a thicker sample [5]. In case of PLA samples, the effect of natural fibre on the reduction in flammability of polymers is clearly seen; the addition of jute reduced the PHRR of PLA by 40%, and sisal by about 20%, Table 2.11. However, the reduction is much less than that shown in PP samples. THR of jute reinforced PLA is higher than PLA, while the lower THR is observed in sisal reinforced PLA which is again due to the lower thickness of the composite. Considering the effect of the polymer matrix on flammability it was found that PLA natural fibre composites, regardless of reinforcing fibre type, consistently displayed lower flammability that the corresponding PP composites. This is due to the superior fire performance of PLA in comparison to PP, Table 2.11. Moreover, the results also show that PLA matrix offered better properties than PP in term of smoke production as the smoke released from natural fibres reinforced PLA composites was almost negligible whereas smoke from PP was much greater.

From all flammability results of natural fibre composites discussed above, it can be summarised that the fire performance of natural fibre composites depends upon the fire properties of materials used both for polymer matrix and reinforcement; Fibre content, fabric area density and thickness of composites should also be considered. In general natural fibres reduce the time-to-ignition (TTI), peak of heat release rate (PHRR), and effective heat of combustion (EHC), but prolong the burning time of the natural fibre composites as compared to their respective neat polymers.

2.4 Methods to improve performances of natural fibre composites

2.4.1 Mechanical performance

As discussed in *Section 2.3.1*, in order to achieve the high mechanical performance of natural fibre composites, it is not only the mechanical properties of materials used for reinforcement and polymer matrix that need to be considered, but also the interfacial adhesion between reinforcing fibres and the polymer matrix. In this section, the commonly used treatments/modifications for improving the fibre/matrix interfacial adhesion of composites reinforced with natural fibres, in particular cellulosic fibres, are discussed.

2.4.1.1 Alkali treatment of natural fibres

Alkali treatment, also known as mercerisation or bleaching, is a well-known process used in textile processing of cellulosic fibres. The mercerisation process exposes cellulosic fibres to a strong alkali solution, i.e. sodium hydroxide (NaOH), in order to remove hemicellulose and lignin from the surfaces of fibres, thus changing the morphology of the some natural cellulosic based fibres by production of rough surfaces on the cell wall of the fibres [87]. In natural fibre composites, the increase in the roughness of the surfaces of fibres after mercerisation is useful

for improving the interfacial adhesion between fibres and matrix by giving rise to additional sites of mechanical interlocking, and promoting more resin penetration at the interface [3,79,88-90]. Prasad et al have studied the effect of mercerisation on the fibre/matrix interfacial adhesion of coconut coir fibre reinforced unsaturated polyester composites [79]. The results showed that the mercerisation improved the tensile properties of the composites with approximately 40% increase in tensile modulus, and 15% in tensile strength. Similar observations, where mercerisation improved the flexural properties of flax reinforced epoxy composites, in particular flexural modulus, by about 30% has been reported by Van de Weyenberg et al [89]. Bisanda et al have reported that the mercerisation also improved the compressive strength of natural fibres composites [90]. They have prepared the sisal reinforced epoxy composites from the fibres which were mercerised with 0.5 N NaOH solution for 72 h. The results showed that the compressive strength of composite from mercerised sisal fibres was improved by about 20% as compared to those from the non-mercerised fibres.

2.4.1.2 Silane treatment

Silane is one of the common coupling agents that has been widely used to modify the surface characteristics of a substrate [77]. The chemical structure of silane has a bi-functional group, Figure 2.13, which could interact with two different phases, of which the surface characteristics are different.

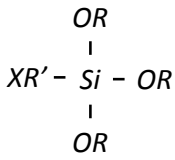

Figure 2.13: Generic structure of silane chemicals where *R*: alkoxy, *X*: an organofunctionality, and *R*′: an alkoxy bridge (or alkoxy spacer) connecting between silicon atom and the organofunctionality.

The bi-functional structure of silane is interesting to apply onto cellulosic fibres to modify its surface characteristic, and improve the compatibility with a polymeric matrix. With the rich hydroxyl groups on the surfaces of cellulosic fibres, the alkoxy groups (*R*) in silane structure can chemically react with these reactive hydroxyl groups through hydrogen bonding in the presence of water, and leave the group of organofunctionality (*X*) on the outer surface of treated fibres, Figure 2.14 [77,91].

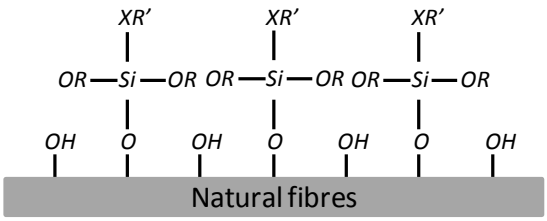

Figure 2.14: The hydrogen bonding between silane and natural fibres

As a result of the presence of organofunctionality on the surfaces of treated fibres, the surface characteristic of the fibres is changed improving the interfacial adhesion between fibres and polymer matrix through either physical or chemical interaction [77,80,81]. The efficiency of silane to improve the fibre/matrix interfacial adhesion depends upon the compatibility and reactivity between the polymer matrix and organofunctional groups of silane. The selection of silane chemical is important factor to maximise its efficiency. The selection of silane type is usually related to the chemical structure of the targeted polymer matrix as their functionalities vary from one to another. The examples of selective silane agents and its suitable polymer matrix system are listed in Table 2.12.

Table 2.12: Examples of potential silane chemicals for natural fibre composites, and their targeted polymer matrices [77]

Chemical structure	Functionality	Target polymer matrix
$(OR)_3$-Si-R'-NH_2	Amino	Polyethylene Polypropylene Polyacrylate Polyvinyl chloride Epoxy
$(OR)_3$-Si-$CH=CH_2$	Vinyl	Polyethylene Polypropylene Polyacrylate
$(OR)_3$-Si- R'-CH_3	Alkyl	Polyethylene Polypropylene Natural rubber
$(OR)_3$-Si- R'-$OC(CH_3)C=CH_2$	Methacryl	Polymethyl methacrylate Polyacrylate Polyester
$(OR)_3$-Si-C_6H_4-SO_2-N_3	Azide	Polyethylene Polypropylene Polystyrene

The effect of silane treatment on the mechanical properties of flax reinforced epoxy composites has been studied by Van de Weyenberg et al [89]. Prior to laminate preparation, flax fibres are treated with 1 wt-% solution of 3-aminopropyl trimethoxysilane in a mixture of water and acetone (50/50 by volume) by immersing the fibres in the silane solution for 2 h, followed by drying in an oven at 80^{o}C for 8 h. The mechanical properties of laminates from untreated and silane treated flax fibres showed that the silane treatment improved the flexural modulus of the composites from 18 GPa to 26 GPa which is about 45% increase. Similar observation was carried out by Gonzalez et al [92]. They reported that the mechanical properties of HDPE (high density polyethylene) composites reinforced with henequen natural fibres (*agave fourcroydes*) were increased after treating the fibres with vinyl tris(2-methoxyethoxysilane) solution containing 1 wt-% silane and 0.5 wt% dicumyl peroxide in the mixture of methanol and water (90/10 by weight) prior to laminate preparation. They also explained that the dicumyl peroxide added in the silane solution also helped to increase the degree of chemical reaction between organofunctionality of the silane and the polymer matrix. Sever et al have investigated the

mechanical properties of polyester composites reinforced with jute fabrics treated with different concentrations of γ-methacryloxypropyl trimethoxysilane (MPS) solutions [93]. The results showed that the mechanical properties, both tensile and flexural properties, of jute reinforced unsaturated polyester composites were increased with the application of MPS treatment on jute fabrics. The concentrations of the applied MPS solution also affected the properties as the improvement in mechanical properties of jute reinforced polyester was further increased when treating jute fabrics with higher concentration of MPS solution.

2.4.1.3 Acetylation of natural fibres

Acetylation is a process used in textile applications to minimise the un-favoured moisture absorption (hydrophilic properties) of cellulosic fibres [3,77]. This technique is therefore useful for the reduction in hydrophilic character of natural fibres, which would enhance the compatibility towards hydrophobic polymers, and hence increase the fibre/matrix interfacial adhesion in composites. In the acetylation process natural fibres are soaked in acetic anhydride solution in acidic condition to substitute hydroxyl groups on surfaces of cellulosic fibres with acetyl groups (CH_3COO-), hence reducing the hydrophilic character of cellulosic fibres. Mishra et al have studied the effect of acetylation on the mechanical properties of sisal reinforced unsaturated polyester composites [94]. Sisal fibres were soaked in acetic anhydride containing one drop of concentrated sulphuric acid for 5 min, followed by water rinsing and air-drying at room temperature. Both treated and untreated fibre reinforced composites were evaluated for their tensile and flexural properties. Results showed that with acetylation the tensile and flexural strength of the composites increased by about 10% in comparison to composites reinforced with untreated fibres. Bledzki et al treated flax fibres with acetic anhydride for different periods of time before fabricating flax reinforced PP composites. On comparing the tensile and flexural properties of composites reinforced with treated and untreated flax fibres, the results showed that mechanical properties of composites from treated fibres were higher than those from the untreated ones, and the mechanical properties increased by about 25% on increasing the treating time from 1 h to 2 h [95].

2.4.1.4 Plasma treatment

Plasma treatment is a technique used for modifying the surface characteristic of substrates by exposing them to the high energy of a plasma flame. With this process, a number of changes in surface characteristics could be achieved, such as surface energy, generation of reactive free radicals, and production of rough surface [3]. In natural fibre composites, plasma treatment is usually used to modify surface and morphology of natural fibres in order to improve the fibre/matrix interfacial adhesion of composites. Many researchers have studied the relationship between surface properties of atmospheric plasma treated natural fibres and mechanical properties of derived composites [96-100]. They have reported that the plasma treatment significantly changes the surface characteristic of natural fibres with the production of roughness and formation of small molecules of oxidised species on the surfaces of treated

fibres. As a result of the changes in surface characteristics, the fibre/matrix interfacial adhesion is enhanced which is mainly due to the increase in surface roughness of the fibres giving rise in sites to perform mechanical interlocking with polymer matrix, and hence resulting in an improvement in mechanical properties.

2.4.2. Fire performance

Since the materials used for reinforcement and polymer matrix of natural fibre composites are flammable, flame retardants can be introduced in either one or both components to fire retard the composites prior to laminate preparation. Flame retardants are a group of chemicals, which, when incorporated in a material, reduce its flammability on exposure to fire. In general, flame retardants function in vapour and/or condensed phases, depending upon the functional groups in the chemicals to slow down or stop the combustion process in material. In the vapour phase, flame retardants can work chemically to interfere with the combustion process by quenching the free radicals generated from a burning material, or physically by diluting the flammable volatiles with production of inert gas from decomposition of flame retardants [43]. Examples of first type are halogen based flame retardants, and of the second type are aluminahydrate, magnesium hydroxide, etc. The condensed phase activity of flame retardants is usually related to interaction between flame retardant and polymer taking place during the decomposition of the polymer in the solid phase. In general, they change the decomposition of the polymer in such a way that more char is formed at the expense of combustible volatiles formation. All phosphorus based flame retardants function in this manner. During burning some condensed phase flame retardants absorb energy to decompose itself, which results in the cooling effect to lower the temperature of the decomposing material, hence further decomposition and burning is stopped [43]. In the following section different flame retardant methods used for different components of the composite are discussed.

2.4.2.1 Flame retardant treatments of natural fibres

The flame retardant treatments for natural fibres, typically cellulosic fibres such as cotton, have been well established for many years. Flame retardants can be simply applied to natural fibres by using textile finishing processes. Pad/dry-cure is one of textile finishing processes that is widely used to apply flame retardants to fibres and fabrics. In the process, fibres/fabrics are impregnated in flame retardant solution, followed by passing through rollers to squeeze out the excess solution. The fibres/fabrics are then dried in an oven to evaporate the solvent, usually water, to obtain non-durable flame retarded fibres/fabrics. To obtain semi-durable, the fabrics can be passed through another oven set at higher temperature (usually 160 - 180^{o}C) for 1 – 3 min to allow a higher degree of interaction between flame retardant and fibres/fabrics [5]. Majority of flame retardants in this group are water soluble salts of inorganic acids [101,102]. Durable flame retardants can also be applied by using the well-known durable flame retardants available for cotton fabrics such as N-methylol dialkyl phosphonopropionamides and tetra-kis(hydroxymethyl)phosphonium. The most commonly used commercial products of these are

Pyrovatex CP and Proban CC respectively [8,102]. In composites, the fibres are however embedded in polymer matrix, therefore durability of flame retardants is not an important issue. Only non- and semi- durable flame retardants, which are water soluble, are therefore discussed here. And, since the natural fibres used in composite application are mostly cellulosic fibres, the examples of common water soluble flame retardants discussed here are from those designed for cellulosic fibres.

Ammonium bromide

Ammonium bromide is a common water soluble halogenated flame retardant that generally works in vapour phase, i.e. pre-flame and flame zones, of the burning materials. On heating ammonium bromide decomposes to ammonia and hydrogen bromide. The released ammonia will work physically to dilute flammable gaseous volatiles liberated from combusted substrates, while hydrogen bromide chemically interferes with the combustion process by inhibiting the initiation of free radicals, and hence slow down or stop the combustion of materials [103,104].

Phosphorus-Nitrogen compounds

In general the chemicals of this type of flame retardant are phosphoric acid salt of organic and inorganic nitrogen containing compounds such as ammonia, guanidine and guanylurea [104]. The well known example of flame retardants in this group are mono- and di-ammonium phosphate (MAP and DAP respectively). These phosphorus (P) and nitrogen (N) containing flame retardants mainly work in condensed phase. When these P-N flame retardants are present in cellulosic fibres they produce phosphoric acid on heating to esterify the cellulose through phosphorylation and form phosphorus ester cellulose [101,102]. The phosphorus ester in cellulose influences the decomposition pathway of cellulose to favour dehydration decomposition (as discussed in *Section 2.1.1.2),* and hence promoting more char formation and less flammable volatiles as compared to untreated cellulose. With the presence of nitrogen, a synergistic action can occur allowing the P based flame retardant to form the crosslinked P-N intermediates which are more reactive phosphorylating agents, and hence providing the better flame retardant efficiency than the related P based flame retardant without the nitrogen [104-106].

Ammonium sulfamate and sulfates

Ammonium sulfamate and sulfates are flame retardant chemicals, which work in the condensed phase. Ammonium sulfamate and sulfates release sulphuric acid upon decomposition, which reacts with hydroxyl groups of cellulosic fibres through a sulfation reaction, thereby changing the decomposition pathway of cellulose. In sulfation, sulphuric acid works as a Lewis acid to esterify cellulose and form the sulphate ester cellulose. This sulphate ester works in a similar way as phosphate ester discussed above, to influence decomposition of cellulose to yield less flammable products and promote better char formation [103,107].

In practice, the use of this technique introducing the flame retardants to natural fibre composites through the reinforcing component has hardly been explored. Only a few works have been published in the literature [108,109]. Matko et al have studied the flammability of flame retarded cellulosic fillers reinforced polyurethane (PU) prepared from wood flakes and corn shell treated with di-ammonium phosphate (DAP) [108]. The fillers were immersed in aqueous solution of DAP, followed by drying under infrared lamp. The ratio between fillers and DAP was kept 1:1 by weight. The flammability of the composites containing 20 wt-% of untreated and DAP treated cellulosic fillers were evaluated by using UL-94 and Limiting Oxygen Index (LOI) tests. In UL-94, the addition of DAP in cellulosic fibres significantly improved the fire performance of the composites from HB (failed to rank in UL-94 vertical classification) to V-0 rating. While, the LOI results showed that DAP dramatically increased the LOI values of the composites from 20 - 23% of non-flame retarded cellulosic reinforced PU to 30% of the flame retarded ones. The flame retardancy of epoxy composites reinforced with coir fibres treated with halogenated flame retardant system, saturated bromine and stannous chloride, has been investigated by Misra et al by using LOI. [109]. With the halogenated treatment, the LOI value of coir fibres reinforced epoxy composites was increased from 36% to 39%.

2.4.2.2 Flame retardant polymer matrix

The Polymer matrix component can be flame retarded by either addition of flame retardant additives, chemical modification of polymer structure, or the combination of both. The incorporation of flame retardant in the polymer matrix is a widely used method for both thermoplastic and thermoset polymers, whereas the chemical modification is favoured for thermoset resin due to the vast choices of resin, curing agents, and hardeners [5]. Common example of modified thermoset resin is the use of halogenated thermoset resin, and the replacement of ordinary curing agents/hardeners with halogenated compounds such as using dichlorostyrene and bromostyrene instead of styrene in unsaturated polyester [1,5,43,110]. Flame retardant additives can be introduced to thermoplastic and thermoset polymer systems by using various techniques. The common process used for mixing flame retardants with thermoplastic polymers is compounding where flame retardant additives and polymer are mixed together in the polymer molten stage by using a twin-screw extruder, similar to the process described in *Section 2.2.1.1*. Flame retardants are often introduced to thermoset resin by mixing with the liquid mixture of resin and curing agent by using a mechanical stirrer prior to casting to solid polymers. There are a number of flame retardants reported in literature for polymers of natural fibre composites fabrication. The examples are ammonium polyphosphate (APP), aluminium hydroxide (ATH), and magnesium hydroxide, and expandable graphite [82,84,86,108,111-116].

Ammonium polyphosphate

Ammonium polyphosphate (APP) has been widely used to flame retard many polymers. The mechanism of APP is similar to that of water soluble P-N flame retardants explained in *Section*

2.4.2.1. On heating APP decomposes and forms polyphosphoric acid. In the condensed phase of combusted polymers, the acid catalyses dehydration reactions and crosslinking to promote more char formation [25,117]. The efficiency of APP varies in different polymers. With the oxygen containing polymers, the efficiency of APP is higher than polyolefin [5,28]. This is due to the reason that polyolefins, i.e. polyethylene (PE) and polypropylene (PP) mostly decompose with no char residue, therefore APP which is a condensed phase flame retardant is less effective [5].

The efficiency of APP to flame retard natural fibre composites has been investigated by many researchers [82,84,108,111-114]. Le bras et al report the use of APP in flax reinforced PP (Flax/PP) composites [82]. The composites of Flax/PP (60/40 by weight) and Flax/PP/APP (31/42/23 by weight) were prepared by compounding PP pellets, short flax fibres (20 mm length), and APP powder by using a twin-screw extruder. The cone calorimetric results of these composites tested at 50 kW/m^2 external heat flux showed that TTI, PHRR, and THR of the flax reinforced PP composites were reduced with the addition of APP. Similar observations have been reported by Schartel et al [84]. They have investigated the flammability of flax reinforced polypropylene (30/70 by weight) with and without addition of 25 wt-% of APP in the polymer matrix. The cone calorimetric results showed that APP significantly reduced the PHRR and THR of flax reinforced polypropylene composites by about 40 - 50%, and noticeably increased the charred residue from 11% to 29%. The efficiency of APP has also been studied by Arao et al [111]. On comparing the cone calorimetric results of wood flour/polypropylene composites containing 30% by weight APP and the non-flame retarded composites, the results showed that the addition of APP decreased PHRR and THR of the composites by about 45% and 20%, respectively. The effect of the APP content has been studied by Matko et al [108]. They have produced a corn starch based thermoplastic biopolymer containing APP at 10, 20, and 30% by weight, and characterised the flammability by using limiting oxygen index (LOI). The results showed that the flame retardant efficiency of APP is greater at higher APP content; an increase of the LOI from 33% to 60% was reported when the APP content in the samples was increased from 10% to 30% by weight.

Metal hydroxides

Metal oxides such as aluminium and magnesium hydroxide work by physical mechanism to reduce the flammability of polymers. On heating aluminium and magnesium hydroxide undergo endothermic decomposition at temperature between 180 - 240^{o}C and 330 - 460^{o}C respectively, and release water vapour as shown in Figure 2.15 [28].

$$2\,Al(OH)_3 \xrightarrow{Heat} Al_2O_3 + 3\,H_2O \quad \text{(a)}$$

$$Mg(OH)_2 \xrightarrow{Heat} MgO + 2\,H_2O \quad \text{(b)}$$

Figure 2.15: Decomposition of (a) aluminium hydroxide and (b) magnesium hydroxide

The released water vapour helps to reduce the temperature of the burning polymers as well as diluting the flammable volatiles produced from the pyrolysis of polymers [28]. They can provide effective flame retardant effect only when used at high loading of about 50 - 60% in the polymer matrix [5].

Aluminium hydroxide (ATH) has been used at 40 wt-% addition in the hemp reinforced unsaturated polyester composite by Hapuarachchi et al [86]. They have investigated the flammability of the composites with and without ATH by using cone calorimetry at 50 kW/m^2 external heat flux. The results showed that ATH prolonged the time-to-ignition of hemp reinforced unsaturated polyester from 54 s to 78 s (by about 45%), and reduced the peak of heat release rate from 362 kW/m^2 to 180 kW/m^2. Sain et al have studied the flame retardant effect of magnesium hydroxide when used in sawdust and rice husk cellulosic filled reinforced polypropylene by using limiting oxygen index (LOI) and horizontal burning test (ASTM D 635) [115]. The results showed that by replacing 50% of cellulosic fillers with magnesium hydroxide, the LOI values of the composites was increased from 26% to 35%, and the horizontal rate of burning was significantly reduced from 35 mm/min to 15 mm/min.

Expandable graphite

On heating, expandable graphite undergoes endothermic decomposition, and expands up to 300 times its initial volume [25]. The expanded graphite works as an insulating layer for underlying materials [5,25]. Schartel et al have compared the flammability of flax/polypropylene composites flame retarded with APP and expandable graphite [84]. The cone calorimetric results at 40 kW/m^2 heat flux showed that at the same solid content expandable graphite showed greater flame retardant efficiency shown by 70% reduction of PHRR, while 50% reduction in PHRR was observed in APP flame retarded composites. The greater efficiency of expandable graphite was further supported by UL-94 result where composites containing expandable graphite could pass V-1 rating, but those containing APP failed the test.

2.4.2.3 Surface coating of composites

Surface coating is another effective methodology to render materials flame retardant. A coating layer is applied on the surface of composites to protect the composites from the heat source during burning and slow down or stop the combustion process. One of well known example of coating used for flame retard materials is intumescent coating. On heating, an intumescent coating swells to form a foamed carbonaceous char layer which works as an insulative barrier to underlying materials against flame and heat [1]. The performance of an intumescent coating depends upon the thickness of the coating as the thicker coating provides better flame retardant properties to underlying materials [118]. Another coating that can be used to fire resist composites is flame retardant coating. Flame retardant coating generally contains flame retardant chemicals, such as halogenated or phosphorus based compounds, dispersed in a

binder. In most cases, flame retardant coating is used to inhibit a flame spread of burning materials by the action of flame retardants contained in the coating [119-121]. These flame retardants function in a similar manner as discussed in above sections. Flame retardant coatings are not as effective as intumescent coatings.

2.5 Method of testing flame retardancy

At present, there are a number of tests and standards available to assess flammability and to evaluate the level of fire performance of materials. The testing conditions of these techniques vary depending upon the application where materials are used. Examples of fire testing specified for different applications are surface flame spread test as specified in BS 476 Part 7 for materials used in British railways; room/corner test (ISO 9705) for marine applications; single burning item test (EN 138230), ignitibility and flame spread test (EN ISO 11925-2) for construction. Some of these tests have already been discussed in *Chapter 1*. As initial assessment for research purposes limiting oxygen index and cone calorimetry are used to access flammability of materials. Limiting oxygen index (LOI) is a technique used to determine the ignitibility of materials in term of minimum oxygen concentration materials required to sustain candle-like burning behaviour. Cone calorimetry is used mainly to measure heat release of materials when it burns under force flaming condition. The principle and testing protocols of LOI and cone calorimetry tests will be discussed in more details in *Chapter 3*.

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Chapter 3: Experimental

This chapter discusses the materials and experimental methodologies used for development of high performance flame retardant (FR) natural fibre reinforced composites by using the combination of FR treated fibres and/or polymer matrices with FR treatment. Firstly, materials used for the development of flame retardant (FR) natural fibre composites in this PhD are discussed in details. These include natural fibres and bio/synthetic polymer matrices for the identification of suitable components for FR natural fibre composites, and chemicals used for flame retardant and surface modification treatments to improve the fire and mechanical performances of natural fibre composites. The methods of application of flame retardant and surface modification treatments on the identified composite components (flax, polypropylene (PP), polylactic acid (PLA), and polyfurfuryl alcohol (Furan)) are explained.

3.1 Materials

3.1.1 Natural fibres

Different natural fibres used for the flammability study of components of natural fibre composites were sourced and provided by Tilsatec Advanced Textile Materials and Camira Fabrics Ltd. All fibres were in short staple form. Their properties are given in Table 3.1.

Table 3.1: Details of short staple natural fibres

Short staple fibres	Average fibre length (mm)	Average linear density (Tex)
Flax	130	2.0
Jute	220	3.3
Hemp	90	4.6
Nettle	180	0.5
Cotton	25	0.3
Wool	20	0.2

3.1.2 Polymer matrices

3.1.2.1 Thermoplastic polymers

3.1.2.1.1 Thermoplastic Fibres

Short staple fibres of different bio and synthetic based thermoplastic polymers used to study the flammability of polymer matrix component of natural fibre composites were sourced by Tilsatec Advanced Textile Materials, and are listed in Table 3.2.

Table 3.2: Details of short staple thermoplastic fibres

Fibres	Average fibre length (mm)	Linear density (dTex)
Polypropylene (PP)	60	2.2
Maleic anhydride grafted polypropylene (MA-PP)	100	2.2
Polylactic acid (PLA)	75	3.3
Polyhydroxyalkonate (PHA)	65	3.7
Poly-3-hydroxy butyrate-co-valerate (PHBV)	60	4.2

3.1.2.1.2 Thermoplastic polymer pellets

Details of polypropylene (PP) and polylactic acid (PLA) pellets used for compounding with flame retardant additives in order to develop the flame retardant polymer matrix are given below.

- Polypropylene (PP) pellets: PPHP 511A (SABIC UK Ltd.) having MFR of 25 g/10min, tested at 230^{o}C using 2.16 kg load [1].
- Polylactic acid (PLA) pellets: Ingeo Biopolymer 2003D (NatureWorks LLC, USA) having MFR of 5-7 g/10min, tested at 230^{o}C using 2.16 kg load [2].

3.1.2.2 Thermoset resins

- Unsaturated polyester (UP)

Resin: Crystic 2-406PA (Scott Bader, UK) containing the mixture of phthalic anhydride-based unsaturated polyester, cobalt octoate (<0.2 wt-%), and styrene (35-40 wt-%) [3].

Catalyst: Catalyst M (Scott Bader, UK) containing butanone (<1.5 wt-%) and methyl ethyl ketone peroxide (30-35 wt-%) dissolved in methyl ethyl ketone [4].

- Epoxy (Ep)

Resin: Araldite LY5052 (Huntsman Advanced Materials Ltd.) containing epoxy phenol novolac (60-72 wt-%) and butanedioldiglycidyl ether (34-42 wt-%) [5].

Hardener: Aradur CH5052 (Huntsman Advanced Materials Ltd.) containing isophorone diamine (30-42 wt-%), 2,2-dimethyl-4,4 methylene bis(cyclohexylamine) (50-56 wt-%), and 2,4,6-tris(dimethylaminomethyl) phenol (1-7 wt-%) [6].

- Polymethyl methacrylate (Acrylic)

Resin: Crestapol 1212 (Scott Bader, UK) containing 2-hydroxyethyl methacrylate (<2 wt-%), methyl methylacrylate (35-40 wt-%), and styrene (6-8 wt-%) [7].

Catalyst: Butanox LPT (Akzo Nobel) containing methyl ethyl ketone peroxide (35 wt-%), diisobutyl phthalate (60 wt-%), and methyl ethyl ketone (2 wt-%) [8].

• Poly(furfuryl alcohol) (Furan)

Pre-accelerated poly(furfuryl alcohol) resin was supplied by NetComposites.

3.1.3 Woven fabrics

Woven fabrics (4x4 basket weave structure) of flax, commingled flax/PP (50/50 wt-%) and commingled flax/PLA (50/50 wt-%) were supplied by Composites Evolution (UK). Details of fabrics are given in Table 3.3:

Table 3.3: Details of flax, flax/PP and flax/PLA woven fabrics

	Flax	Flax/PP	Flax/PLA
Ends / cm	9	9	9
Picks / cm	11	11	11
Linear density of warp yarn (Tex)	218.1	216.0	237.9
Linear density of weft yarn (Tex)	219.5	218.7	239.3
Crimps of warp (%)	1.0	4.6	3.0
Crimps of weft (%)	4.4	6.7	4.0
Fabric thickness (mm)	1.3	1.8	1.4
Warp cover factor	13.3	13.2	13.9
Weft cover factor	16.3	16.3	17.0
Fabric cover factor	29.6	29.5	30.9
Actual area density (g/m^2)	467	465	493
Calculated area density (g/m^2)	450	460	494
% difference between actual and cal. area density	3.6	1.1	0.2

3.1.4 Chemicals for scouring treatment

All chemicals, listed below, were reagent grade with at least 98% purity, and supplied by Fisher Scientific UK Ltd.

• Sodium hydroxide (NaOH), 98% purity.

• Sodium carbonate (Na_2CO_3), 99.5% purity.

• Sodium phosphate tribasic (Na_3PO_4), 98% purity.

• Acetic acid (CH_3COOH), 99.7% purity.

3.1.5 Flame retardants

3.1.5.1 Flame retardants for woven fabrics

The commercial flame retardants containing different chemicals as listed in Table 3.4 were supplied by Thor Specialities Ltd. as concentrated solutions, except mono-ammonium phosphate which was supplied in the powder form.

Table 3.4: Details of flame retardants supplied by Thor Specialities Ltd

Flame retardant	Solid Cont. (wt-%)	N (%)	P (%)	S (%)	Br (%)
Ammonium sulfamate (AS)	42	10.2	-	7.7	-
Ammonium bromide (AB)	54	11.6	-	-	15.5
Guanidine dihydrogen phosphate (GDP)	42	10.6	9.2	-	-
Guanylurea methylphosphonate (GUP)	50	14.0	8.6	-	-
Mono-ammonium phosphate (AP)	100	27.3	2.5	-	-
Inorganic phosphate (IP)	54	17.6	6.8	-	-

Note: N, P, S and Br contents were provided by manufacturer (Thor Specialities Ltd.)

3.1.5.2 Flame retardants for thermoplastic fibres (PP and PLA)

Three different phosphorus based flame retardants (FRs) were sourced from different sources. The details of the FRs are given in Table 3.5.

Table 3.5: Flame retardants for preparation of FR-PP and FR-PLA fibres

Flame retardant types	Chemical composition	Melting temperature (^{o}C)	P Cont. (wt-%)	N Cont. (wt-%)
NP	Organic nitrogen-phosphorus compound	-	14	37
OP	Organic phosphorus compound	> 245^{o}C	24	-
ZP	Zinc phosphinate	200^{o}C	20	-

Note: Due to the commercial sensitivity of these flame retardants, their actual chemical compositions, trade names and suppliers are not provided

3.1.5.3 Flame retardants for thermoset resin (furan resin)

• Resorcinol bis(diphenyl phosphate) (RDP).

• Bisphenol A bis(diphenyl phosphate) (BAPP).

• 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO).

• Ammonium polyphosphate (APP).

• Melamine polyphosphate (MPP).

Due to the commercial sensitivity of the developed flame retardant furan resins and their derived composites, the details of commercial grades and suppliers of these flame retardants are not provided.

3.1.6 Chemicals for surface modification to improve fibre/matrix interfacial adhesion

• Vinyl triethoxysilane (deposition grade with ≥98% purity), supplied by Sigma Aldrich.

• 3-aminopropyl triethoxysilane (reagent grade with 99% purity), supplied by Sigma Aldrich.

• Dicumyl peroxide (reagent grade with 98% purity), supplied by Sigma Aldrich.

• Ethanol (technical grade with purity of 96% v/v), supplied by VWR International.

3.2 Sample preparation

3.2.1 Polymer plaques preparation

3.2.1.1 Thermoplastic polymers

Plaques of thermoplastic polymers were made by using compression moulding technique. 100 g of the short staple fibres of each thermoplastic polymer were placed between two aluminium plates. The aluminium plates were sprayed with releasing agent before use to ensure easy removal of the sample after pressing. A square frame made of metal plates of 3 mm thickness, with internal area of 17.5 cm x 17.5 cm was placed on one aluminium plate. 100 g of the short staple fibres were placed in the mould and covered with another large aluminium plate. The assembly was then heated at a set temperature specific to each polymer type as specified in Table 3.6 for 150 s under 40 kg/cm^2 pressure in a hot press machine (Daniels Upstroking Press with 10 inches diameter ram, TH&J DANIELS ltd.). After 150 s the assembly was removed from the hot press and transferred to a water - cooled press (Moore Hydraulic Upstroking Press with 4 inches diameter ram, Moore ltd.) Pressure was applied again, 20 kg/cm^2 this time, until the sample had cooled to ambient temperature. After that the assembly removed from the press and polymer plaque sample removed from the plates.

Table 3.6: The processing temperatures of thermoplastic polymers

Polymer	Processing Temperature (^{o}C)
Polypropylene (PP)	180
Maleic anhydride grafted polypropylene (MA-PP)	180
Polylactic acid (PLA)	180
Polyhydroxyalkonate (PHA)	160
Poly-3-hydroxy butyrate-co-valerate (PHBV)	170

3.2.1.2 Thermoset resins

Plaques of thermoset resins were prepared by using casting technique. A 100 g mixture of thermoset resin and the respective catalyst/hardener at the mass ratio required for each resin system (see Table 3.6) were mixed together in a 250 ml beaker, and then stirred by a glass rod until the homogeneous dispersion was achieved. The well-dispersed mixtures were then poured into 100 mm x 100 mm square moulds to obtain 3 mm depth of the liquid mixture, and then cured to plaques by heating in a laboratory oven at a temperature as required for each resin system by using the curing cycle as shown in Table 3.7.

Table 3.7: The formulations and curing cycles of thermoset resins

Sample	Formulations (wt-%)			Curing cycles		
	Resin	Catalyst/Hardener		Step 1	Step 2	Step 3
UP	98	2	Temp.	RT	80°C	-
			Time	24h	6h	-
Ep	70	30	Temp.	RT	80°C	-
			Time	24h	6h	-
Acrylic	98	2	Temp.	RT	80°C	120°C
			Time	24h	5h	3h
Furan	100	-	Temp.	60°C	90°C	140°C
			Time	12h	6h	1h

Note: RT is room temperature

3.2.2 Fabric treatments

3.2.2.1 Scouring treatment

Scouring is a process that is usually used for pre-treating fabrics containing cellulosic fibres in order to remove the impurities and waxes presented in the fibres prior to applying any finish for textile related applications. As a result of the removal of impurities and waxes, scouring also increases fabric wettability and hence pick up of the finish [9]. In this work, woven fabrics of flax, flax/PP and flax/PLA were scoured with an alkali solution by immersing the fabrics in a glass container containing the alkali solution at a required temperature for a required period of time (details are given in *Chapter 5*). The scoured fabrics were subsequently neutralised by immersing in a 0.5 wt-% acetic acid solution, followed by rinsing with water before drying in a laboratory oven at 80°C for 1 h. The masses of the fabrics before and after scouring treatment were recorded, noted as W_{Ori} and $W_{Scoured}$ respectively, and calculated for the percent mass loss of fabrics after scouring treatment by using Equation 3.1.

$$Weight\ loss\ of\ fabric\ (\%) = \frac{(W_{Ori} - W_{Scoured})}{W_{Ori}} \times 100$$

Equation 3.1: Weight loss of fabric after scouring treatment

3.2.2.2 Flame retardant treatment

Pad/dry which is one of the most commonly used methods for fabric finishing for textile applications was used to apply flame retardants onto the woven fabrics. To flame retard the fabrics, a flame retardant solution was firstly prepared by adding a flame retardant (listed in *Section 3.1.4.1*) in water to achieve a desired concentration, and stirring with a glass rod until completely dissolved. The fabrics were then passed through a bath containing the prepared flame retardant solution, followed by passing through padding rollers, where 20 psi pressure is applied on the rollers, to squeeze the excess of flame retardant solution out of the fabrics as shown in Figure 3.1. The treated fabrics were then allowed to dry in a laboratory oven at 100°C.

Figure 3.1: Flame retardant treatment of fabrics by using a laboratory padder

The weight of the fabrics before/after FR treatment was also recorded, and calculated for the percent FR uptake of the FR treated fabrics by using Equation 3.2.

$$FR\ uptake\ of\ fabric\ (\%) = \frac{(W_{FR\ fabric} - W_{Untreated\ fabric})}{W_{FR\ fabric}} \times 100$$

Equation 3.2: Flame retardant (FR) uptake of fabric after FR treatment

3.2.2.3 Atmospheric pressure plasma treatment

Plasma treatment is a well-known technique used for modifying the surface characteristics of substrates [13]. With the plasma treatment, a variety of surface modification can be achieved, e.g. increase of surface energy, introduction of free radicals onto surfaces, and production of rough surfaces due to an etching effect [10,11]. In this work, atmospheric pressure cold plasma was used for treating flax/PP and flax/PLA fabrics. The details of this apparatus are given elsewhere [12], which consists of a plasma containment quartz tube, placed into a Surfatron microwave cavity. This is connected with a SAIREM microwave generator operating at 2.45 GHz with a maximum continuous power output of 300 Watts. The illustration of the apparatus taken from Ref. [12] is presented in Figure 3.2. To generate a plasma flame, argon gas (99.99% purity) with a flow rate of 15 L/min is fed into a fused quartz reactor chamber, and ignited by striking by using a copper wire. The surfaces of flax/PP and flax/PLA fabrics on both sides were exposed to plasma flame at different plasma flame intensities (50, 100, and 150 kW) under air atmosphere, and a scanning speed of 3 min/100 cm^2. The distance between the nozzle of the plasma quartz tube and the fabrics was kept at 20 mm.

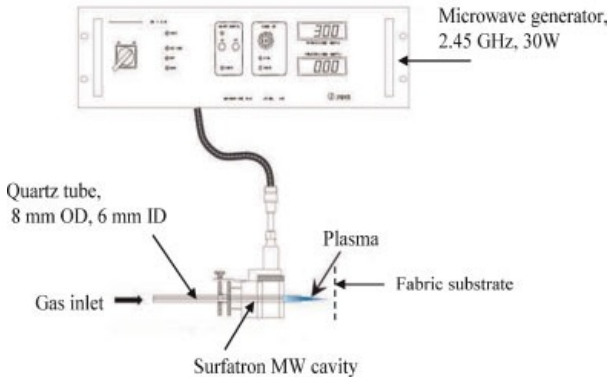


Figure 3.2: Schematic of the atmospheric pressure cold plasma apparatus [12]

3.2.2.4 Silane treatment

The vinyltriethoxysilane (VTS) and 3-aminopropyl triethoxysilane (APTES) solutions were prepared at different concentrations (1, 2, and 3 wt-%) by adding the required type of silane (VTS or APTES) into the mixture of water and ethanol (20/80 wt-%), and then stirring by using a glass rod until completely dissolved. The flax/PP and flax/PLA woven fabrics were treated with these VTS and APTES solutions. The solution was sprayed onto both sides of the fabrics by using a spray bottle until the fabric was completely wet with the silane solution. The silane treated fabrics were then heated to 80^{o}C in a laboratory oven for 12 h. The weights of fabrics before and after treatments were also recorded for calculation of the percent silane content on the fabrics by using same calculation as for FR uptake in Equation 3.2.

3.2.2.5 Combination of silane and plasma treatments

In this treatment technique, the procedures of plasma and silane treatments discussed above were used for treating flax/PP and flax/PLA woven fabrics. The woven fabrics were firstly treated on both sides with the plasma flame at 150 kW intensity by using the procedure described in *Section 3.2.2.3*, followed by immediate spraying of the 3 wt-% silane solution (VTS and APTES for flax/PP and flax/PLA, respectively) as described in *Section 3.2.2.4.* These treated fabric samples were then heated to 80^{o}C in a laboratory oven for 12 h, followed by the plasma treatment again at 150 kW plasma flame intensity on both sides of the fabrics.

3.2.3 Flame retardant thermoplastic fibres

• *Compounding of flame retardant PP and PLA*

To prepare the FR-PP and FR-PLA samples, the mix of polymers and flame retardant additives were melt compounded by using a Thermo electron Prism Eurolab 16 XL twin-screw extruder (Thermo Fisher Scientific Inc.), Figure 3.3.

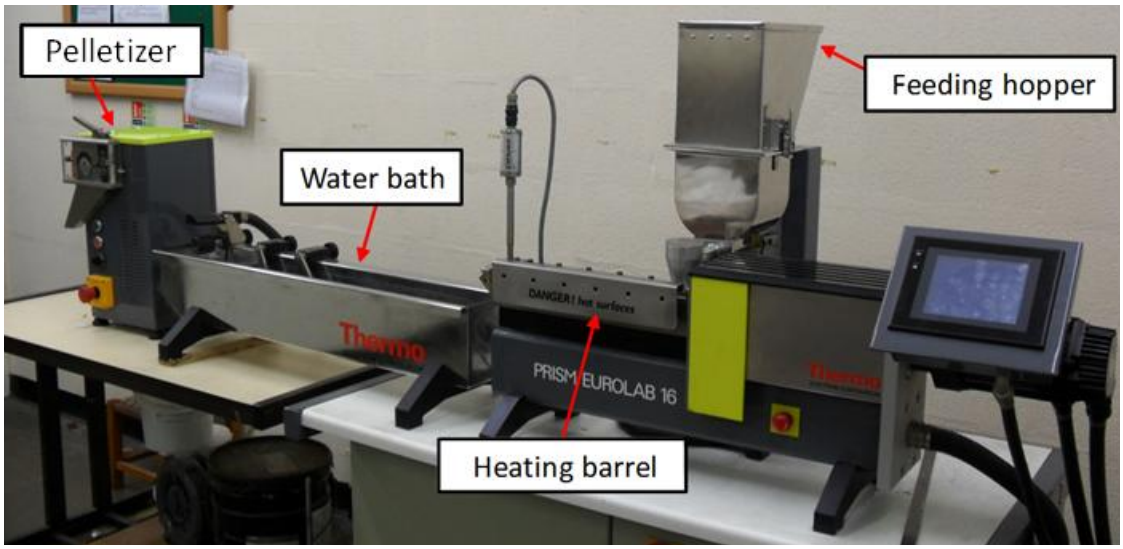


Figure 3.3: Thermo electron Prism Eurolab 16 XL laboratory twin-screw extruder

The polymers (PP and PLA) and flame retardants (listed in *Section 3.1.4.2*) were physically mixed together in a plastic container by using a glass rod, and then transferred to a feeding hopper of the twin-screw extruder to extrude to strands by using the temperature profile (^{o}C) from the feeder to the nozzle zones as presented in Figure 3.4. The extruded strands were then cooled down by passing through a water bath, and passed through a pelletizer to form small pellets.

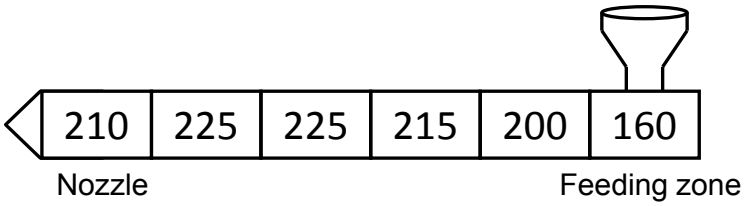


Figure 3.4: Temperature profile (^{o}C) of a twin-screw extruder for compounding FR-PP and FR-PLA

• *Fibre extrusion*

The control and compounded FR containing samples of PP and PLA were melt-extruded into continuous filaments by using a FET pilot plant scale fibre extruder (Fibre Extrusion Technology Ltd., UK), Figure 3.5. All PLA containing compounded samples were dried in a laboratory oven at 50^{o}C for 12 h prior to extrusion, since the high moisture content in the samples could cause partial degradation of PLA during the processing at high temperature.

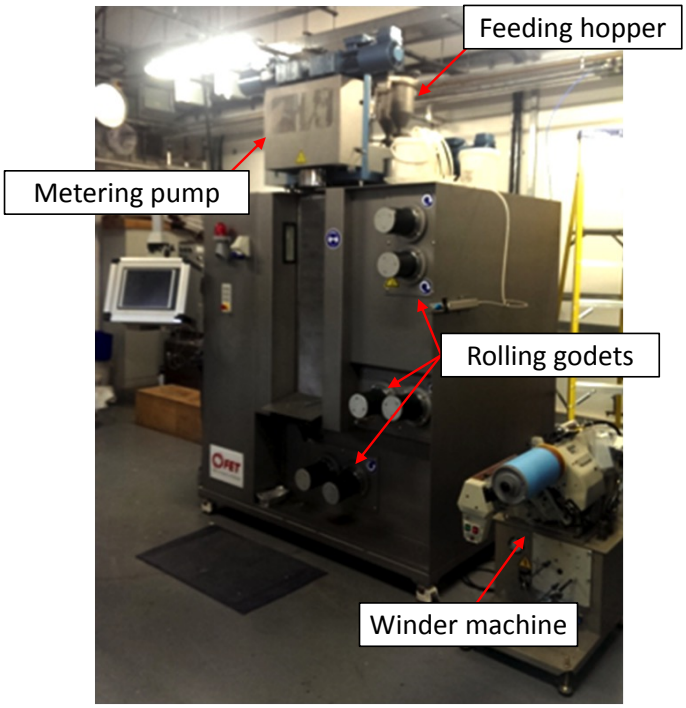


Figure 3.5: Fibre Extrusion Technology (FET) melt-spinning fibre extruder

The dried pellets were introduced to the FET fibre extruder through the feeding hopper, and then transferred through the barrel of the extruder where the heating bands are located to melt the pellets at the temperature required for each type of polymer, 230^{o}C and 250^{o}C for PP and PLA samples respectively. The molten samples were then conveyed to the spinneret head to extrude to filaments through a 20 holes (800 µm diameter) spinneret die by a metering pump in order to control a feeding speed of molten polymer, and to obtain a steady pressure at the spinneret die head. The extruded filaments were cooled down by using an air quench operating at 15^{o}C and 20 m^{3}/s flow rate, followed by an application of a spin finish (L5277JU containing triglyceride and antistatic agent, Fibre Extrusion Technology UK). The filaments were subsequently drawn by using three sets of heated godets for which the temperature and rotating speed of the godets were varied depending on the properties of filaments of each sample in order to draw the filaments without breaking. Finally, the filaments were wound on to a package by using a Leesona winder machine.

3.2.4 Preparation of flax reinforced furan (flax/Furan) prepregs

Prepregs of the control and flame retardant flax/furan were produced from untreated or FR treated flax woven fabrics and control or FR containing furan resin by using a prepreging machine at NetComposites (UK). Details of the samples are given in *Chapter 8.*

3.2.5 Composite preparation

3.2.5.1 Flax reinforced thermoplastic laminates (flax/PP and flax/PLA)

Three different types of control and flame retarded flax/PP and flax/PLA composite, single, two and eight layered laminates, were prepared from control, flame retarded woven flax/PP and flax/PLA fabrics. The required layers of the 17.5 cm x 17.5 cm fabrics for each type of laminate were placed between two aluminium plates, which were sprayed with release agent beforehand, without the use of a spacer. The assembly was melt-pressed by using a hot press machine (Daniels Upstroking Press with 10 inches diameter ram, TH&J DANIELS ltd.) at 175^{o}C for 150 s under 30 kg/cm^{2} pressure, and then transferred to a cold press (Moore Hydraulic Upstroking Press with 4 inches diameter ram, Moore ltd.) with cooled plates under 20 kg/cm^{2} pressure until the sample had cooled to ambient temperature.

3.2.5.2 Flax reinforced thermoset laminates (flax/Furan)

The control and flame retarded flax/furan prepregs, prepared by using the procedure described in *Section 3.2.4,* were cut to 30 cm x 30 cm sizes. Six layers of the prepregs were placed between two PTFE sheets. The assembly of stacked layers of prepregs and PTFE sheets was then pressed between two aluminium plates at 140^{o}C under the pressure of 20 kg/cm^{2} for 40 min by using a hydraulic upstroking press (Moore ltd.), and then cooled down to ambient under the same pressure.

3.3 Testing and characterisations

3.3.1 Thermal stability characterisation

Thermal stabilities of flame retardants, polymers, and composite laminates were studied by using thermogravimetric analysis (TGA). TGA is a characterisation technique by which the mass of a substance, heated at a controlled rate is recorded as a function of time or temperature. The atmosphere can be varied from air to inert gases such as nitrogen. In this work, the thermal stability of the samples was studied in two modes, dynamic (ramping from room temperature to a required temperature) and isothermal (at a particular temperature for a required period of time), by using SDT2960 simultaneous DTA-TGA (TA Instruments).

• *Thermal stability study by using dynamic mode of TGA*

A sample with the mass of 5-10 mg was heated from room temperature to 700^{o}C, unless otherwise stated elsewhere, by using a heating rate of 10^{o}C/min under air atmosphere with 100 ml/min flow rate. The mass of the samples was recorded as a function of the temperature to produce the mass loss curves of the samples. The data from the mass loss curves were analysed for the thermal stability of the samples by determining the onset of decomposition, the temperature at a maximum decomposition rate, percent mass residue at different temperatures/times, etc.

• *Thermal stability study by using isothermal mode of TGA*

This test was performed to study the thermal stability of FRs at the laminate processing temperature (200^{o}C) was selected for both PP and PLA samples. A sample (5-10 mg) was heated to 200^{o}C by using the heating rate of 20^{o}C/min under air atmosphere flowing at 100 ml/min, and then isothermally holding the temperature for 20 min. The mass of the samples at the evaluated temperature was recorded to produce mass loss curves as a function of time. The data was used to measure any mass loss occurring for 20 min.

3.3.2 Surface morphology and chemistry characterisations

3.3.2.1 Fourier Transformed Infrared (FTIR) spectroscopy

The chemical characteristics on the surfaces of flax/PP and flax/PLA fabrics before and after treatments were studied by using FTIR spectroscopy analysis in the attenuated total reflectance (ATR) mode by using Thermo Scientific IS10 Nicolet FTIR spectrometer coupled with the smart iTR accessory. The absorbed IR spectra of the samples were collected in the range of the wavelength between 600 and 4000 cm^{-1}.

3.3.2.2 Scanning electron microscopy (SEM)

The surface morphologies of flax/PP and flax/PLA fabrics were analysed by using scanning electron microscopy (SEM). The fabric samples, 10 mm x 10 mm sizes, were mounted on a stub by using SEM conductive adhesives tape. The sample mounted on the stub was then placed in the chamber of Polaron Range SC7620 Sputter Coater to coat with a conductive layer of gold by exposing for 45 s of plasma exposition. The surfaces of coated fabric samples were then observed through a Hitachi S3400-N scanning electron microscope by using an acceleration voltage of 5 kV.

The fractured surfaces of composite laminates after tensile or flexural testing were also studied by the SEM. The small samples were carefully cut to ensure no damage occurs on the fractured surfaces. The sample was mounted on a stub by placing the fractured surface upward, and gold coated by using procedure explained above. An acceleration voltage of 10 kV was used for SEM analysis of these samples.

3.3.3 Flammability testing

3.3.3.1 Limiting oxygen index (LOI)

Limiting oxygen index is a well-known technique used to determine the flammability of materials by measuring the minimum concentration of oxygen, expressed as a percentage by volume of oxygen in the flowing mixture of oxygen and nitrogen gaseous, that will sustain candle liked burning behaviour in a material [13,14]. According to the standard procedure of LOI test

described in ISO 4589, a bar shaped specimen, sized 12.5 mm x 100 mm with the thickness of 3 mm, is ignited at the top of specimen by using an ignition gas flame which is withdrawn from the specimen once an ignition of specimen has occurred. The burning time of the ignited specimen at different oxygen concentrations is recorded in order to determine the minimum oxygen concentration that the specimen requires to sustain burning for at least 3 min after removal of the ignition flame [14].

• *Limiting oxygen index of natural fibres*

There is no standard procedure of sample preparation and testing method available to evaluate the LOI values of fibres. In this work, a methodology was therefore developed. A bundle of 10 cm length and 5 g mass of each natural fibre had a metal wire wound around it, and tightened in between a sample holder as shown in Figure 3.6. With this sample preparation, the natural fibres are therefore able to be tested for their LOI values according to the standard procedure described above. A Fire Testing Technology (FTT) Limiting Oxygen Index analyser was used.

Figure 3.6: Sample preparation of natural fibres for LOI testing

• *Limiting oxygen index of polymer plaques*

The test specimens were cut from the polymer plaques to a standard size of 12.5 mm width and 100 mm long as specified in ISO 4589, and then tested for their LOI values by using the standard procedure described above.

3.3.3.2 UL-94 test

UL-94 is one of the most commonly used flammability test, especially in industrial applications, for determination of the burning behaviour of materials in terms of ignitibility of materials when exposed to a 20 mm height small flame by giving classification of V-0, V-1 and V-2 by using UL-94 vertical burning test (details are discussed below). In case that material cannot be ranked in the vertical classification, the horizontal rate of burning is then determined by using horizontal burning test.

• *Vertical burning test*

A specimen of 150 mm x 13 mm with a thickness of 3 mm is marked at 25, 75 and 125 mm from the end of specimen where a flame is applied. The specimen is clamped vertically, and subjected to a 20 mm height flame of a Bunsen burner by keeping a constant distance between the end of specimen and the top of the Bunsen burner at 10 mm. A thin layer of indicator cotton is positioned 300 mm below the test specimen in order to catch molten drops that may drip from the specimen during the test as shown in Figure 3.7.

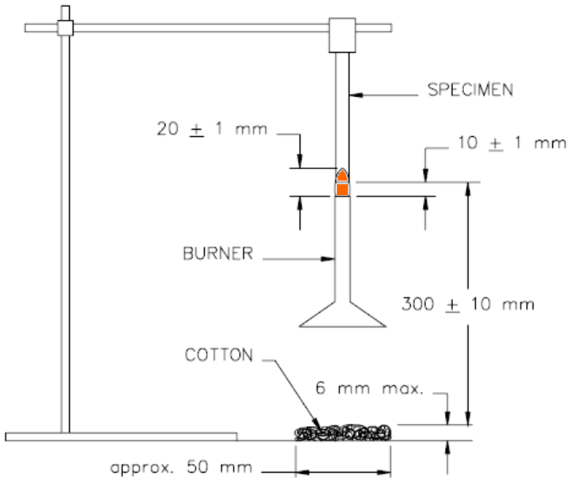


Figure 3.7: The schematic of UL-94 vertical burning test [15]

The flame is applied at the bottom end of the specimen for 10 s, and then the burning time of the specimen after removal of the flame is noted (t_1). If the specimen extinguishes before burning up to the sample holder, the flame is applied again for another 10 s. The burning time of the specimen after the second flame application is noted (t_2). During the test, if the cotton is ignited by the flaming drops from the tested specimen, that is also recorded.

From this, if the specimen burns longer than 30 s or burns up to the sample holder after the removal of the flame application, it is classified as fail in vertical burning test. Otherwise, the vertical rating classification of the specimen is justified by using the criteria given in Table 3.8.

Table 3.8: Criteria of UL-94 vertical rating classifications [15]

Classification	Afterflame time after each of the removal of the ignition flame (t_1 and t_2)	Ignition of the indication cotton caused by molten drops
V-0	<10s	No
V-1	<30s	No
V-2	<30s	Yes

In this work, the burning times when the flame reaches each timing mark of the specimen were also recorded. Since the length of the burnt sample is known, the vertical rate of burning of materials can be calculated by using Equation 3.3.

$$Burning\ rate\ (mm/min) = \frac{Burnt\ length\ (mm)}{Burning\ time\ (s)} \times 60$$

Equation 3.3: The burning rate calculation of UL-94 tested specimen

• *Horizontal burning test*

A specimen with the same size as described in the vertical test, marked with three timing lines at 25, 75 and 125 mm from the end of specimen, is clamped with its transverse axis inclined at 45 degrees as shown in Figure 3.8. A Bunsen burner (20 mm height flame) is then applied at the free end of the specimen for 30 s or until the flame reaches the first timing mark at 25 mm from the edge. If the flame extinguishes before reaching the first timing mark, after removal of the Bunsen burner, the sample is termed as self-extinguished. If the specimen continues burning, the time when the flame reaches each timing mark is recorded, and calculated for the horizontal burning rate by using Equation 3.3.

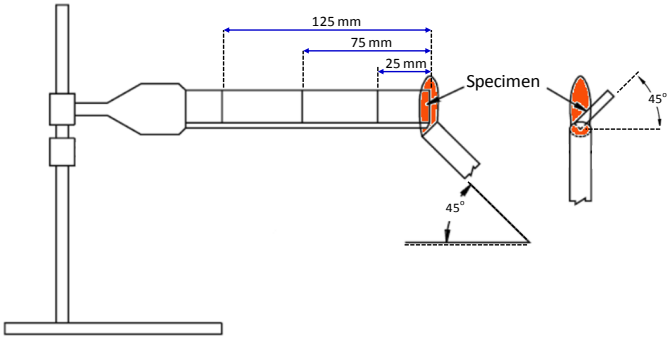


Figure 3.8: The schematic of UL-94 horizontal burning test [15]

3.3.3.3 Cone calorimetry

The fire performances of polymer plaques and composite laminates have been investigated by using a Fire Testing Technology (FTT) cone calorimeter, Figure 3.9.

Figure 3.9: Fire Testing Technology (FTT) cone calorimeter

The details of the cone calorimetric test are available in ISO 5660. The size of specimen in the standard is defined as 100 mm x 100 mm with a minimum thickness of 3 mm [16]. The specimens are mounted on a sample holder, which is placed on a load cell to detect the mass of the sample during the test, and then exposed to a radiant conical heat source in horizontal orientation at radiant pre-determined heat flux. A spark ignition source is situated at 13 mm above the top of a specimen. The distance between the cone heat source and the top surface of the specimen is kept at 25 mm. The exhaust duct of the cone calorimeter is set at 24 L/s flow rate to extract the volatiles generated from the tested samples, and then feeding into an oxygen analyser to measure the amount of oxygen that was consumed during the combustion of the samples. Since the principle of the cone calorimetry is based on the theory that most fuels generate approximately 13.1 MJ of heat release per 1 kg of oxygen consumed [17], the measured amount of the consumed oxygen during the combustion of the tested samples is therefore converted to the amount of heat energy released from the samples by using a vender cone calorimeter software (ConeCalc, Fire Testing Technology). The smoke released from the tested samples is also measured by determining the smoke opacity in the exhaust duct of the cone calorimeter with respect to light transmittance of a laser (632.8 nm wavelength) to a photocell detector located cross the duct [16]. During the test, time to ignition (TTI) and flame out time (FOT) of the tested specimen, timed from the moment the sample is first exposed to the heat source.

In this work, the specimens sized 75 mm x 75 mm with a thickness of about 3 mm were tested in triplicate for each sample by using the standard testing procedure as described above. Heat fluxes of 35 and 50 kW/m^2 were used for testing thermoplastic and thermoset samples respectively. In previous work in our laboratory, a comparative study on the flammability of two different sizes of samples has been undertaken [18]. The results have shown that when the surface area of the specimen is reduced from the standard size of 100 x100 mm^2 to 75x75 mm^2, the similar PHRR, THR and EHC results of the same sample are obtained. Different parameters provided by cone calorimeter were therefore used to assess the flammability of the polymer plaques and composite laminates in this work. These include time to ignition (TTI), flame out time (FOT), heat release rate (HRR, kW/m^2), peak of heat release rate (PHRR, kW/m^2), and total heat released (THR, MJ/m^2), total smoke released (TSR), percent char residue and etc.

3.3.4 Fibre/matrix interfacial adhesion testing

To investigate for the fibre/matrix interfacial adhesion of natural fibre composites, a peeling test technique was developed, which is based on the ISO 11339 standard used for flexible-to-flexible bonded assembly [19]. Specific sample preparation was required to produce two layered composite laminates with ends free for gripping and eventually peeling. Two fabric strips of flax/PP and flax/PLA with 125 mm length were partly wrapped with PTFE tape for 25 mm length from the edge of the strips prior to laminate preparation in order to partly bond two layers

together, and leave the un-bonded ends for gripping with an Instron Universal tester during the experimental setup of a peeling test as shown in Figure 3.10.

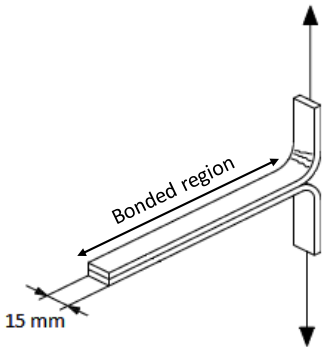
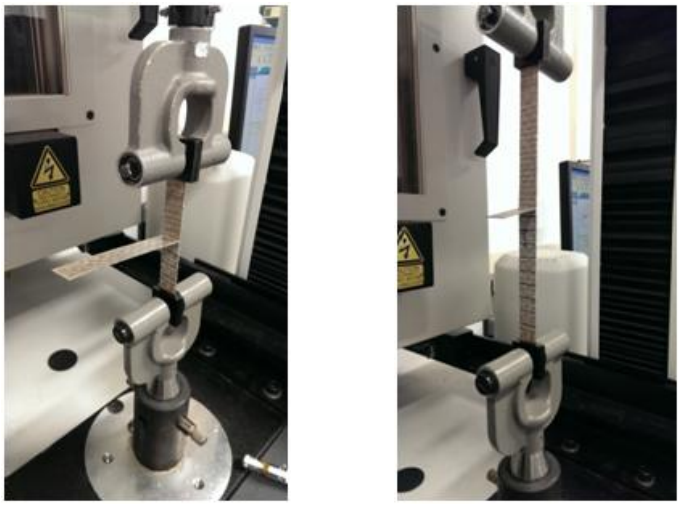


Figure 3.10: A two layered composite laminate for peeling test

The two layered flax/PP and flax/PLA laminates were tested for the peeling strengths by using an Instron 3369 Universal tester. The test was conducted by clamping each un-bonded end of the specimen firmly in the grips of the Instron, Figure 3.11 (a), and peeling the bonded region off with a 100 N load cell at a crosshead speed of 50 mm/min.



(a) ***(b)***

Figure 3.11: Images of the specimen (a) before and (b) after peeling test

The load (N) and displacement (mm) was recorded, termed as the peeling force and grip separation distance in this setup. From this, the curve of peeling force versus the distance of grip separation was produced, an exemplar curve is shown in Figure 3.12. From the curve, the average peeling strength was then calculated after disregarding the peeling force of first and last 25 mm of the grip separation distance.

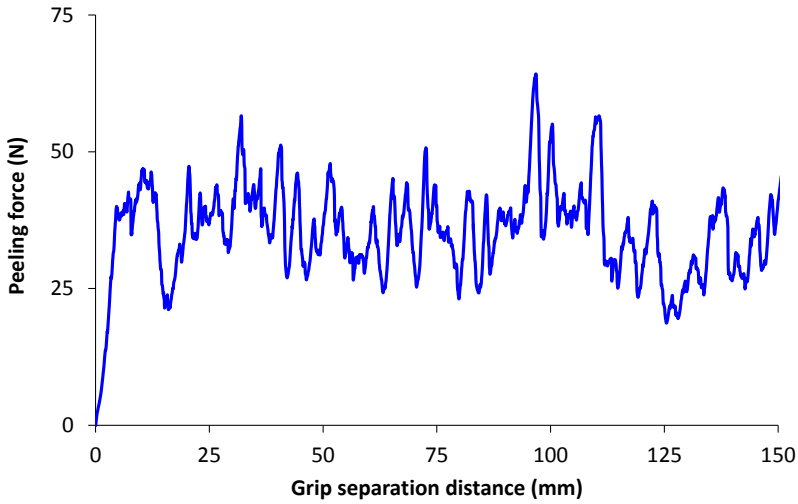


Figure 3.12: Peeling test result of two layered flax/PP laminate (peeling force versus grip separation distance)

3.3.5 Mechanical testing

The mechanical properties of the control and flame retardant natural fibre composite (flax/PP, flax/PLA and flax/Furan) laminates were evaluated in three different modes; tensile, flexural and impact.

3.3.5.1 Tensile test

The control and FR treated composite laminates were characterised for tensile properties by using an Instron 3369 Universal tester in accordance with BS EN ISO 527 [20]. Three replicated specimens of the size of 150 mm x 20 mm x 3 mm were tested for each sample. Prior to the test, both ends of a specimen were bonded with polymeric tab by using high stretch adhesive glue, Figure 3.13, to ensure failure within the gauge region.

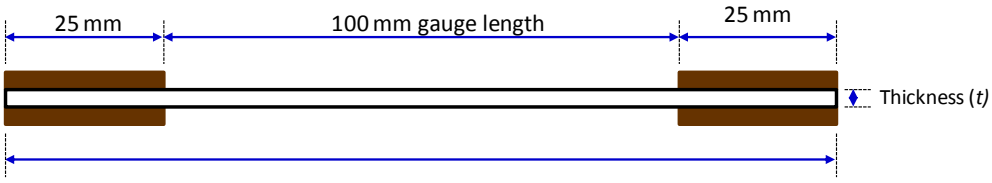


Figure 3.13: Tensile test specimen

The tensile test was performed by using Instron 3369 and 50 kN load cell, and a crosshead speed of 1 mm/min. During the test, the load and displacement of the tested specimen were recorded by using a built-in data acquisition of Instron 3369 in order to produce a tensile load-displacement curve for calculation of the tensile modulus ($E_{Tensile}$) of the specimen by using Equation 3.4. From the curve, the maximum load was also noted for the tensile strength of the specimen.

$$E_{Tensile} = \frac{L}{wt}K$$

Equation 3.4: Formula for a tensile modulus calculation, where L = gauge length, w = width and t = thickness of the specimen; K = an initial stiffness of a specimen determined from the slope taken from the elastic region of load-displacement curve.

3.3.5.2 Flexural test (three-points bending)

Flexural properties of the laminates were investigated by using a three point bending test according to the standard procedure specified in BS EN ISO 14125 [21]. Three replicate specimens of the same sizes as specified in tensile test (see *Section 3.3.5.1*) were tested each sample.

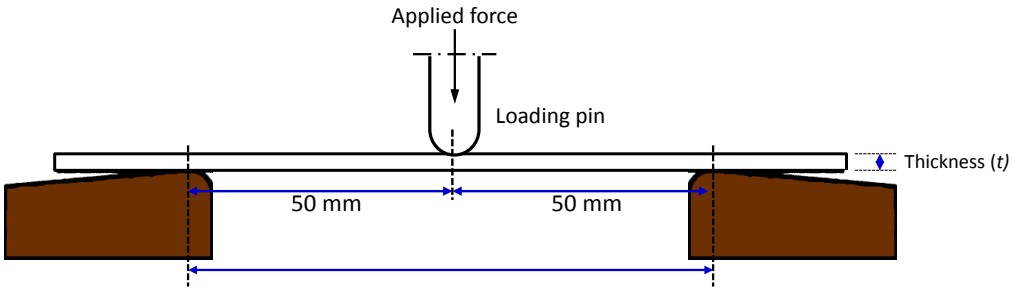


Figure 3.14: Flexural test of composite laminates [24]

The test was conducted by using an Instron 3369 Universal tester in a displacement controlled mode with a 50 kN load cell. A specimen with the same size as used for tensile test was placed on the supporter with the adjusted span length of 100 mm, Figure 3.14. The specimen was then bended by applying load through the loading pin at the middle of specimen with a displacement rate of 1 mm/min in depth. The load and displacement of the tested specimen were recorded, from which the load-displacement curves were drawn. From the curve, the flexural modulus was calculated by using Equation 3.5 [21], and the load at maximum before failure of the specimen was noted as flexural strength.

$$E_{Flex} = \frac{L^3}{4wt^3}K$$

Equation 3.5: Formula for a flexural modulus calculation, where L = span length between the supports; w = width and t = thickness of the specimen; K = an initial stiffness of the specimen determined from the slope of load-displacement of the tested specimen in the elastic region.

3.3.5.3 Impact drop weight test

The impact properties of the control and FR treated laminates were investigated by using an Instron Dynatub Mini-Tower drop weight impact machine in accordance with ASTM D7136 [22]. The samples, sized 75 mm x 75 mm, were firmly clamped on the samples holder, which has a hole (76.2 mm diameter) in the centre. And then the clamped samples were impacted by dropping a steel impactor of 16 mm crosshead diameter, and 1.03 kg weight from 100 mm

height to produce the impact energy of 3.4 J on the sample. A high-speed data acquisition system (Dynatup® Impulse™ software data capture system) was used to collect data from the impact test, from which the impact load-defection curves of the tested samples were produced. From the obtained load-defection curves, the impact modulus (E_{Impact}) of each sample was calculated by using Equation 3.6.

$$E_{Impact} = \frac{3D}{4\pi h^3} K$$

Equation 3.6: Formula for an impact modulus calculation, where D = the diameter of the hole of the sample holder; h = thickness of the specimen; K = an initial stiffness of the specimen determined from the slope in the elastic region of the load-defection curve.

3.4 References

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[20] BS EN ISO 527-5:2009 Plastic – Determination of tensile properties Part 5: Test conditions for unidirectional fibre-reinforced plastic composites

[21] BS ISO 14125:1998+A1 Fibre reinforced plastic composites – Determination of flexural properties

[22] ASTM D 7136 Standard Test Method for Measuring the Damage Resistance of a Fiber-Reinforced Polymer Matrix Composite to a Drop-Weight Impact Event

Chapter 4: Flammability of components of natural fibre composites

In this chapter flammability of different natural fibres and bio/synthetic polymers has been studied in order to identify suitable inherently flame retardant components for producing high performance flame retardant natural fibre composites. The natural fibres selected for testing were flax, jute, hemp, nettle, cotton and wool. Their flammability in fibre form has been studied by limiting oxygen index (LOI).

For the polymer matrix component, a number of thermoplastic and thermoset polymers have been tested. The selection criteria of the polymers was that the processing temperature should be lower than the onset of decomposition temperature of natural fibres (approximately 200^{o}C [1]). Thermoplastics included polypropylene (PP), maleic-anhydride grafted polypropylene (MA-PP), polylactic acid (PLA), polyhydroxybutyrate (PHB), and poly-3-hydroxy butyrate-co-valerate (PHBV). Unsaturated polyester (UP), low temperature curing grade epoxy (EP), acrylic, and poly(furfuryl alcohol) (Furan) resins were chosen for thermoset polymers. Plaques of thermoplastic and thermoset polymers were prepared by using melt-pressing and casting techniques, respectively, as discussed in Chapter 3 (see *Section 3.2.1*). Limiting oxygen index (LOI), UL-94 and cone calorimetry techniques were used to evaluate flammability of these materials.

4.1 Flammability of natural fibres

There is no standard procedure available for testing the LOI of fibres [2], therefore a methodology of sample preparation and a testing protocol were developed in this study as discussed in details in *Section 3.3.3.1*. Bundles of 100 mm long natural fibres were wound with metal wire in order to hold the fibres vertically for conducting the LOI test as specified in the standard test method (ISO 4589). The LOI results of different natural fibres are reported in Table 4.1. During the test, all cellulosic fibres, flax, jute, hemp, nettle and cotton behaved very differently as compared to the thermoplastic and thermoset materials. Prior to burning like a candle as specified in the LOI standard test, they smoulder at oxygen concentrations lower than that required for flaming mode. During smouldering although a flame is not seen, the sample keeps decomposing and disintegrating until the entire sample is consumed. Therefore, the LOI values of these cellulosic fibres were noted in both smouldering and flaming behaviours. While the flaming mode is similar to that in the ISO standard, the smouldering LOI is the minimum concentration of oxygen required for the sample to combust to carbonaceous char without the presence of flame.

Table 4.1: Limiting oxygen index (LOI) of natural fibres

Sample	Limiting oxygen index (%)	
	Smouldering mode	Flaming mode
Flax	20.0	26.2
Jute	21.0	22.8
Hemp	16.8	26.6
Nettle	16.8	31.6
Cotton	15.6	18.8
Wool	-	26.4

The LOI results presented in Table 4.1 show that in the flaming mode, nettle fibres have the highest LOI value of 31.6%, followed by flax, hemp and wool fibres which have a similar LOI of about 26%. The cotton fibres show the lowest LOI of 18.8%. On comparing the LOI results in smouldering mode of different cellulosic fibres, the results did not show the same trend as observed in the flaming mode. The two highest LOI values in the smouldering mode were observed for jute and flax fibres, showing the value of 21.0% and 20.0% respectively, followed by hemp, nettle and cotton. Wool on the other hand did not smoulder. Considering the LOI results in both flaming and smouldering modes, wool can be considered as the least flammable with the LOI of 26.4% in flaming mode. And then the next one is flax with the LOI of 20.0 and 26.2% in smouldering and flaming modes respectively.

The difference in flammability properties of these fibres can be explained due to the difference in chemical compositions of the fibres. All cellulosic fibres generally consist of highly crystalline cellulose fibrils in a matrix of amorphous phase of hemicellulose, lignin, pectin and waxes. Each of these components has different thermal stability, and fire properties. Hence the content of these components plays an important role in the flammability of the fibres. The details of compositions of cellulosic fibres have been comprehensively reviewed in *Chapter 2,* and summarised here in Table 4.2.

Table 4.2: Chemical compositions of cellulosic fibres [1,3,4]

Fibre	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Pectin (%)	Waxes (%)
Flax	60-71	14-19	2-3	1.8-2.3	1.5
Jute	51-72	12-20	5-13	0.2	0.5
Hemp	70-75	18-22	2-3	0.8	0.7
Nettle	53-83	6-12	0.5-2	1-5	-
Cotton	92-95	2-6	0.5-1	1-2	0.5-1

The main components of cellulosic fibres that have a significant impact on the flammability of the fibres are cellulose and lignin [1]. On heating, cellulose decomposes to laevoglucosan which can subsequently pyrolyse and yield highly flammable volatiles [1], whereas lignin which is a

highly cross-linked aromatic chemical structure decomposes to less flammable products, and more char formation [1,5]. From this discussion it can be seen that the higher cellulose content, the more flammable a cellulosic fibres is. Cotton which contains about 92-95% cellulose of its chemical compositions is therefore the most flammable natural fibre in comparison to the others. Flax, jute, hemp and nettle consisting of less cellulose and higher lignin contents (Table 4.2), are less flammable as shown by the higher LOI values of these fibres as compared to that of cotton fibres, Table 4.1. The chemical composition of wool fibre is totally different from cellulosic fibres as it is a protein based fibres derived from animal hairs. The main composition of wool is polypeptide of different amino acids (keratin), shown in Figure 4.1, which is a char promoting precursor, and hence wool contributes more to char formation during decomposition in comparison to cellulosic fibres [6,7]. This leads to a relatively high LOI of wool fibres as compared to other natural fibres, in particular cotton which is of high cellulose content.

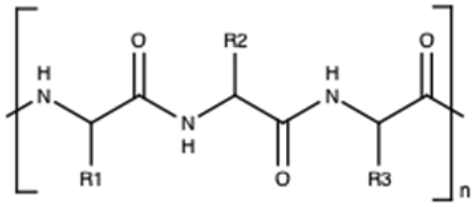

Figure 4.1: The chemical structure of keratin in wool fibres where R_1, R_2 and R_3 are alkyl groups [7]

4.2 Flammability of polymer matrices

4.2.1 Thermoplastic polymers

The LOI results of the thermoplastic polymers are reported in Table 4.3. On comparing the LOI results of the thermoplastic polymers, MA-PP and PP had the lowest LOI values of 17.8 and 18.0% respectively, followed by PHBV, PLA and PHB with the LOI of 18.2, 19.2 and 22.0%, respectively. This is due to the chemical structure of these polymers, Figure 4.2.

Table 4.3: The flammability results of thermoplastic polymers

Sample	LOI (%)	UL-94						
		Horizontal			Vertical			
		B. Time (s)	B. Rate (mm/min)	No. Drops	B. Time (s)	B. Rate (mm/min)	No. Drops	Rating
PP	18.0	164 ±13	37 ±3	570 ±32	44 ±6	146 ±43	305 ±21	Failed
MA-PP	17.8	152 ±10	40 ±3	394 ±12	38 ±7	143 ±10	260 ±8	Failed
PLA	19.2	141 ±5	43 ±2	327 ±9	28 ±2	170 ±63	182 ±5	Failed
PHB	22.0	123 ±7	49 ±3	52 ±10	42 ±1	255 ±35	29 ±6	Failed
PHBV	18.2	134 ±10	46 ±3	552 ±17	114 ±12	50 ±5 *	333 ±10	Failed

* Dripping of molten polymer caused a slow rate of burning

The chemical structure of PP is long molecular chains of propylene repeating unit, Figure 4.2 (a). On heating, due to the low thermal stability of hydrocarbon structure of propylene it readily decomposes and yields highly flammable products [8-10], and hence displayed low LOI values.

To improve the compatibility to PP with other polymers or for surface treatments, usually a small percentage of maleic anhydride grafted polypropylene (MA-PP) is added to the bulk. The MA-PP enhances char formation ability and reduces melt-dripping of PP [10], as also seen in UL-94 results in Table 4.3. When the melt-dripping is reduced, the polymer is held intact for a longer time and hence burns, this results in lowering of its LOI, as can be seen from Table 4.3 where the LOI value is reduced from 18.0% in control PP to 17.8% in MA-PP. On the other hand, PLA, PHB and PHBV, which are bio based polyester polymers, contain oxygen atoms in their repeating units, Figure 4.2 (c) – (e). Due to the presence of oxygen in the structure, they decompose with less flammable products [8,9], and hence show high LOI values as compared to PP and MA-PP.

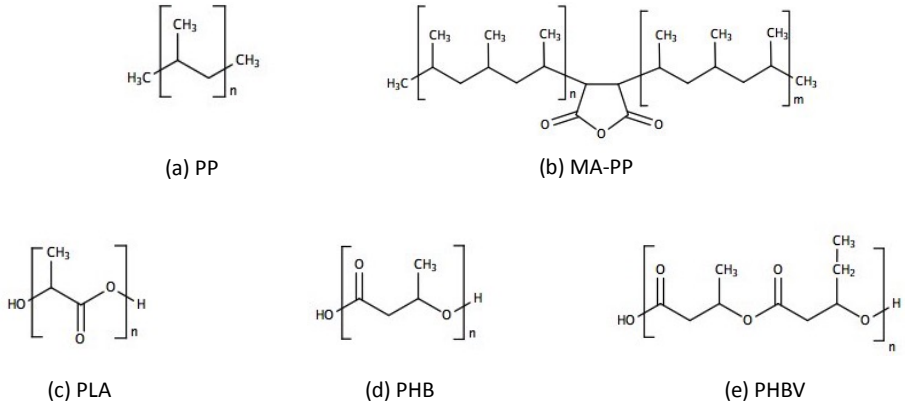

Figure 4.2: Chemical structures of thermoplastic polymers

From Table 4.3, the UL-94 test results of these polymers show that all these thermoplastic polymers failed the vertical rating of UL-94 as the samples were completely burnt up to the sample holder. This was as expected as when comparing the LOI of these polymers to that of the percent oxygen in the atmosphere, theoretically 20.95%, most of them have lower LOI values, hence will easily burn. To have better understanding of the burning behaviour of the thermoplastic polymers, rates of burning in both vertical and horizontal orientation of UL-94 test were also measured. The results are given in Table 4.3. The horizontal rate of burning results showed that PP and MA-PP burned with the lowest burning rate of 37-40 mm/min, followed by PLA, PHBV and PHB respectively. While, in vertical test PHBV burned with the lowest rate of burning, followed by PP, MA-PP, PLA and PHB. These showed that the burning rate results of these samples did not follow the same trend as observed in the LOI results. The polymers having low LOI values (PP, MA-PP and PHBV) performed better with the lower rates of burning compared to the polymers having higher LOI values (PLA and PHB) in UL-94 test. This is due to the fact that in the UL-94 test the melt dripping behaviour of polymers has a significant impact on the rate of burning of the samples as dripping could cause the flame to partially go out from the specimen with drips, and hence the specimen burns with a small flame. The number of drops occurred during the UL-94 test are reported in Table 4.3. The results show that PHBV and PP burned with the highest melt-dripping rates compared to others, followed by MA-PP, PLA and PHB respectively. As a result of the high melt-dripping, PHBV and PP, which although have low LOI values, burned with lower rate of burning compared to others as more flame went

out with the drops. The difference in melt dripping behaviour of these polymer is due to the difference in physical melting characteristic and thermal degradation of these polymers [11,12]. On heating PP decompose to small molecules that have low viscosity, and hence result in high rate of melting dripping during their combustion [11]. With the presence of maleic anhydride in the structure, MA-PP displays less dripping behaviour as compared to neat PP. This is due to the influence of maleic anhydride on the decomposition mechanism of PP to yield more char, hence increased the viscosity and reduced melt-dripping of molten PP during combustion [10]. In bio based polymers, due to the presence of oxygen in their chemical structures, Figure 4.2, they decompose with more char formation, and hence burned with low melt dripping, except PHBV. This is due to PHBV has low glass transition temperature (T_g) of about 2^{o}C in comparison to PHB (T_g = 25^{o}C) and PLA (T_g = 60^{o}C) [13], and hence on heating PHBV melt to low viscosity molten polymer and showed high rate of melt-dripping as seen in Table 4.3

The flammability of the thermoplastic polymers was also investigated by using cone calorimetry at 35kW/m^2 external heat flux as described in *Section 3.3.3.3.* The curves of heat release rate (HRR), rate of smoke release (RSR) and mass loss as a function of time are graphically presented in Figure 4.3. The derived results from these curves are numerically reported in Table 4.4.

Table 4.4: Cone calorimetric results of thermoplastic polymers at 35 kW/m^2

Sample	TTI (s)	FOT (s)	T_{PHRR} (s)	PHRR (kW/m^2)	THR (MJ/m^2)	EHC (MJ/kg)	TSR (L)	Yield (%)
PP	41 ±1	160 ±1	143 ±4	1819 ±106	115 ±2	47 ±1	1445 ±51	3.1 ±1.5
MA-PP	45 ±3	166 ±1	130 ±6	1430 ±134	94 ±15	46 ±2	1208 ±243	9.8 ±7.4
PLA	46 ±1	179 ±12	131 ±1	677 ±64	58 ±1	18 ±1	22 ±3	2.4 ±1.9
PHB	38 ±1	160 ±7	107 ±1	773 ±43	67 ±3	21 ±1	226 ±38	11.5 ±0.1
PHBV	40 ±1	128 ±3	99 ±4	1283 ±48	65 ±1	21 ±1	405 ±38	3.1 ±0.4

The cone calorimetric results of two commonly used synthetic thermoplastic polymers (PP and MA-PP) for natural fibre composites in Table 4.4 showed that PP ignited at 41 s, and burned with very high peak heat release rate (PHRR) of 1819 kW/m^2, producing 115 MJ/m^2 total heat release (THR). The effective heat of combustion of PP is 47 MJ/kg. During combustion, PP also released large amount of smoke shown by the high total smoke release (TSR) of 1445 L. Whereas, maleic anhydride grafted polypropylene (MA-PP) ignited slightly later than PP at 45 s, and burned with PHRR of 1430 kW/m^2. In comparison to PP, MA-PP has with lower THR and EHC of 94 MJ/m^2 and 46 MJ/kg, respectively. And also, mass loss curves presented in Figure 4.3 (c) show that MA-PP produced increased char residue of 9.8% as compared to 3.1% of PP. This indicated that MA-PP has better fire performance than PP shown by the lower PHRR and THR; plus higher char residue, although it shows lower LOI value than PP, due to its char formation tendency as has been discussed earlier. This observation is in agreement with that reported in literature where the grafting of maleic anhydride onto PP improved the thermal stability of PP by slowing down its rate of decomposition and promoting more char formation, and hence reduced the flammability of PP [10,14].

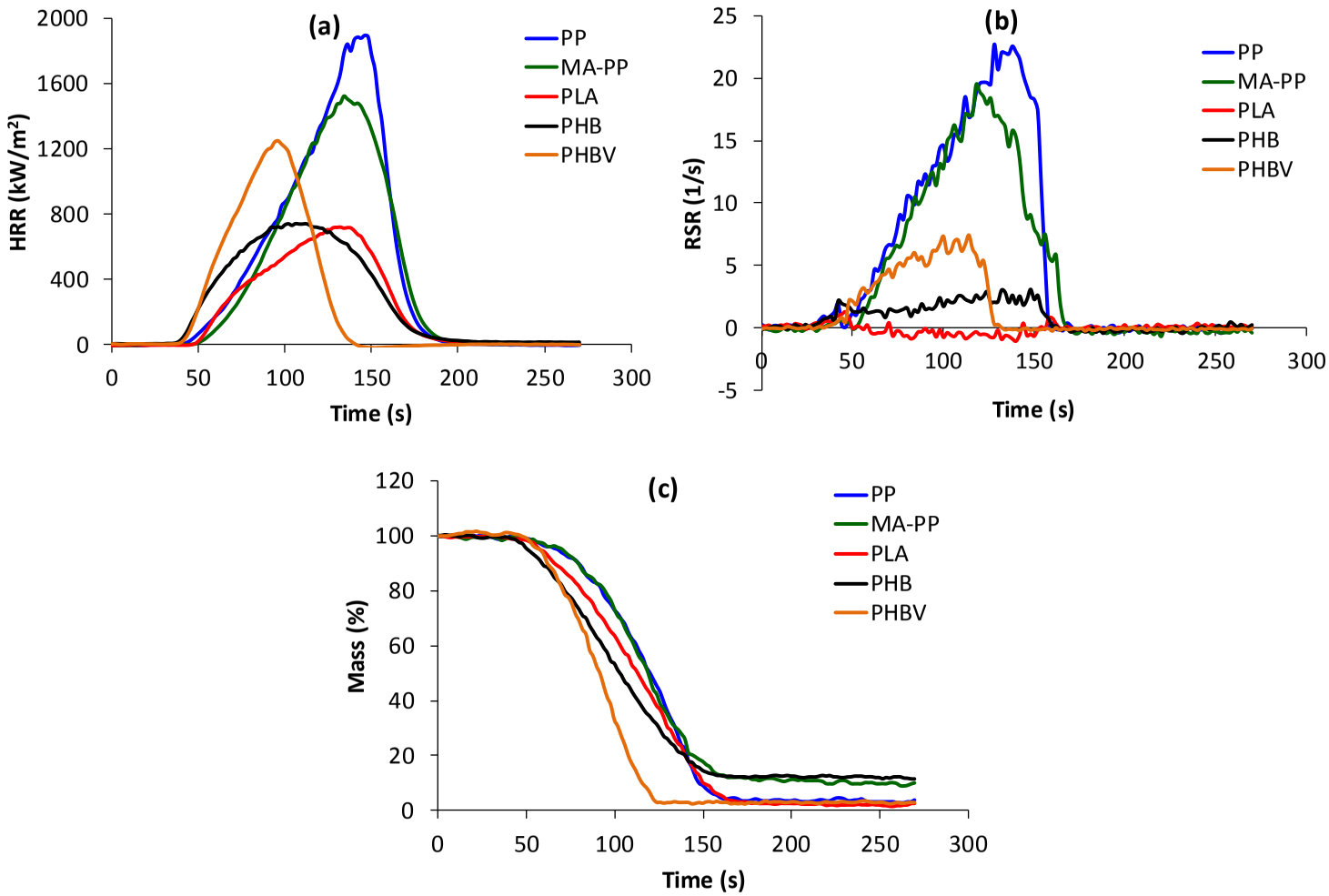

Figure 4.3: Cone calorimetric results of thermoplastic polymers tested at 35 kW/m^2 external heat flux: (a) heat release rate (HRR), (b) rate of smoke release (RSR), and (c) mass loss curves as a function of time

For bio based thermoplastic polymers of PLA, PHB and PHBV, as expected due to the low LOI value PHBV exhibited lower fire performance than others. PHBV ignited at 40 s, and burned with high PHRR of 1283 kW/m^2 producing THR of 65 MJ/m^2 and TSR of 405 L. The EHC of PHBV is 21 MJ/kg. The results of PHB show that it ignited at 38 s, and burned with much lower PHRR of 773 kW/m^2 in comparison to PHBV. The THR and EHC of PHB are however similar to that of PHBV as although PHB burned with much lower PHRR, its burning time was longer as compared to PHBV, Figure 4.3 (a). PHB produced less smoke (TSR = 226 L). It also produced more char (11.5%) in comparison to PHBV. PLA shows longest time-to-ignition (TTI) as compared to others (46 s), and burned with very low PHRR of 677 kW/m^2 producing THR of 58 MJ/m^2. PLA also shows low TSR and EHC of 22 L and 18 MJ/kg, respectively.

All the flammability results discussed above indicate that in general bio based thermoplastic polymers (PLA, PHB, and PHBV) are less flammable than the synthetic ones (PP and MA-PP). And, on comparing between these thermoplastic polymers, their fire performance can be ranked as: PLA > PHB > PHBV > MA-PP > PP. Although the actual decompositions of polymers are complex, when considering the fire performance of these polymers in relationship to their chemical structures, Figure 4.2, the generic trend can be seen here that the polymer with high content of alkyl groups and less functionality (i.e. ester group) in the chemical structure of its repeating unit is more flammable. The reason being that when polymer pyrolyses the alkyl groups produce highly flammable molecules, whereas the presence of oxygen in ester group influence polymer to decompose and yield less flammable products [8]. As can be seen from Figure 4.2, PLA contains ester group and less alkyl groups in its structure as compared to others, hence shows least flammability properties as can be seen from its relatively high LOI; lowest PHRR, THR and EHC.

4.2.2 Thermoset polymers

Plaques of different thermoset resins were tested for their flammability by using LOI, UL-94, and cone calorimetry at 50 kW/m^2 external heat flux. The LOI and UL-94 results of the resins are reported in Table 4.5. The LOI results showed that furan resin (biopolymer) had the highest LOI of 39.8%, and then followed by low temperature curing grade epoxy (EP), acrylic and unsaturated polyester (UP) resins with the LOI of 22.4, 21.4 and 18.6% respectively.

Table 4.5: The flammability results of thermoset resins

Sample	LOI	UL-94				
		Horizontal		Vertical		
	(%)	B. Time (s)	B. Rate (mm/min)	B. Time (s)	B. Rate (mm/min)	Rating
UP	18.6	287 ±16	21 ±1	39 ±4	155 ±17	Failed*
EP	22.4	322 ±39	19 ±2	26 ±3	232 ±25	Failed*
Acrylic	21.4	300 ±32	20 ±2	56 ±6	108 ±11	Failed*
Furan	39.8	-	-	-	-	V-0**

* Sample completely burned to a sample holder (100 mm length) during UL-94 testing
** Sample did not ignite during UL-94 testing

The superior fire performance of furan resin in comparison to others could be explained by its aromatic structure. While the structure of UP, EP and acrylic resins with the crosslinked structure of unsaturated ester moities; diepoxide and diamine; and methyl methacrylate, respectively, furan resin is a crosslinked network of furfuryl alcohol monomers, which has an aromatic structure of 5 membered ring as shown in Figure 4.4 [15,16]. This aromatic structure provides high thermal stability to the furan resin, and on heating it decomposes to less flammable products, thereby showing low flammability properties [8,9].

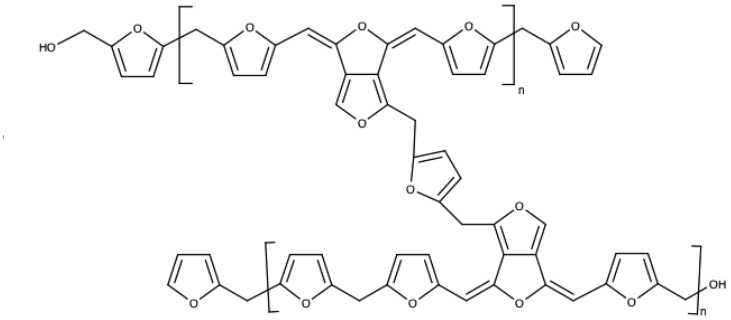

Figure 4.4: Chemical structure of crosslinked poly(furfuryl alcohol) (furan resin) [16]

The UL-94 results in Table 4.5 show as expected that due to the remarkable high LOI value furan resin was the only resin that could achieve V-0 rating in UL-94 vertical classification as the sample did not ignite during the testing, whereas the other resins failed the vertical test as the sample completely burned up to the sample holder. In UL-94 test, the horizontal and vertical rates of burning of the resins were also measured, and are reported in Table 4.5. The results show that all resins, except furan resin as the sample did not ignite, burned with similar rates of burning of 20 mm/min in horizontal test, but performed different performances in vertical orientation. The vertical rates of burning results showed that EP resin burned with the fastest rate at 232 mm/min, followed by unsaturated polyester (UP) and acrylic resins with the burning rates of 155 and 108 mm/min, respectively.

The HRR, RSR and mass loss curves of the thermoset resins tested at 50 kW/m^2 are presented in Figure 4.5. The derived data from these curves are given in Table 4.6.

Table 4.6: Cone calorimetric results of thermoset resins at 50 kW/m^2

Sample	TTI (s)	FOT (s)	T_{PHRR} (s)	PHRR (kW/m^2)	THR (MJ/m^2)	EHC (MJ/kg)	TSR (Litre)	Yield (%)
UP	32 ±1	165 ±1	107 ±10	1007 ±17	94 ±4	20 ±1	3567 ±153	1.0 ±0.7
EP	42 ±1	163 ±18	117 ±4	1820 ±258	122 ±5	28 ±1	3231 ±107	1.8 ±0.1
Acrylic	36 ±1	607 ±2	79 ±1	643 ±5	109 ±4	22 ±1	2593 ±54	7.1 ±1.5
Furan	84 ±11	171 ±10	112 ±3	613 ±2	26 ±1	10 ±1	57 ±29	46.4 ±1.3

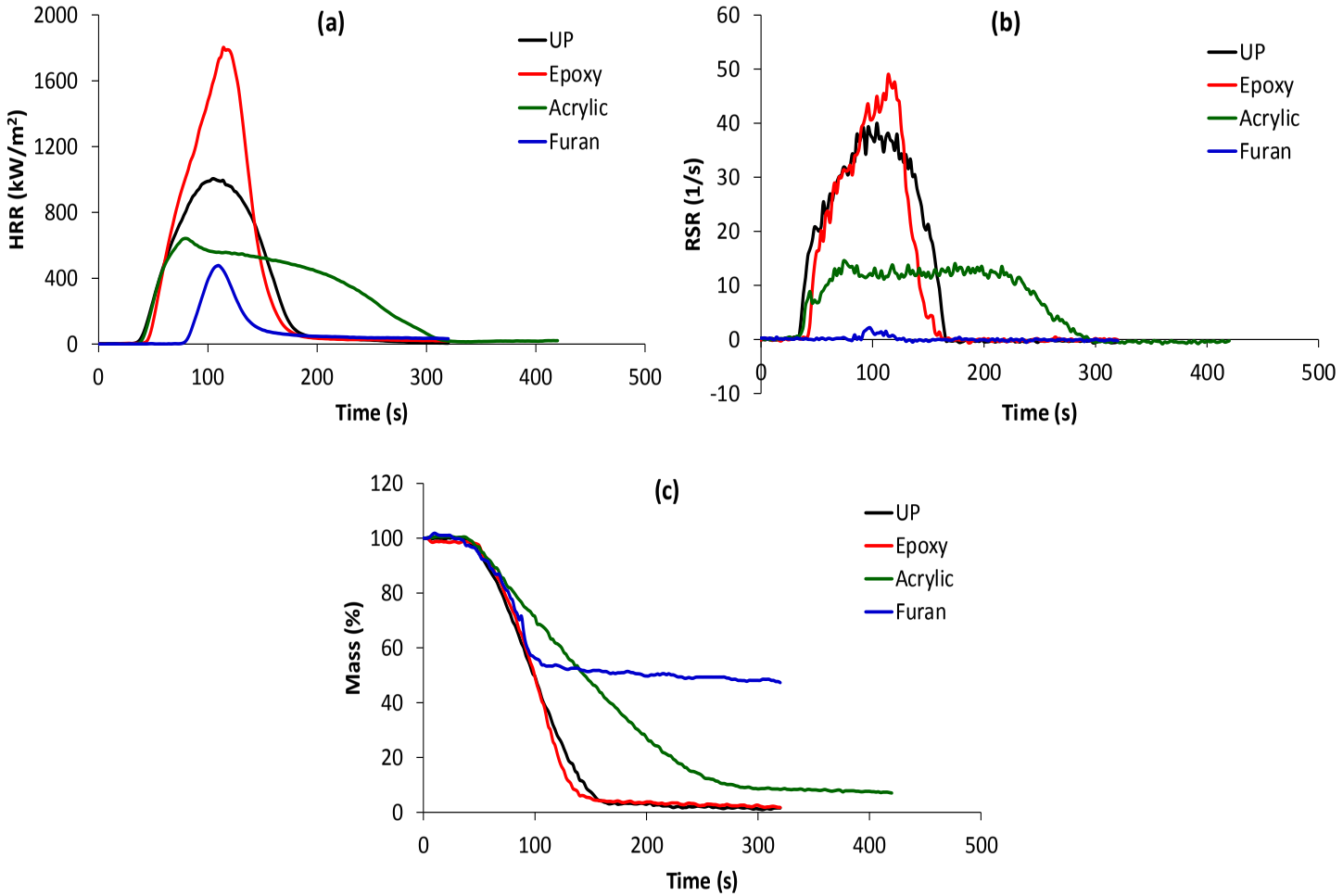

Figure 4.5: Cone calorimetric results of thermoset polymers tested at 50 kW/m^2 external heat flux: (a) heat release rate (HRR), (b) rate of smoke release (RSR), and (c) mass loss curves as a function of time

Similar to the low LOI of unsaturated polyester resin (UP), it shows the shortest time-to-ignition (TTI) as compared to other resins. UP ignited at 32 s after exposure to the cone heat source, and burned with 1007 kW/m^2 PHRR producing 94 MJ/m^2 THR. The EHC of UP is 20 MJ/kg. During burning UP released high volume of smoke of 3567 L. This is due to the presence of styrene, which is well known for smoke generating compound, in UP as a crosslinking agent [15]. The low temperature curing epoxy resin (EP) shows better performance than UP with TTI (42 s). However, once ignited, it burned with very high PHRR of 1820 kW/m^2, and produced THR of 122 MJ/m^2. This leads to the higher EHC (28 MJ/kg) of epoxy, Table 4.6. Smoke production during combustion of EP was similar to that of UP. Acrylic resin, results show that it ignited at 36 s, and slowly burned with low PHRR (643 kW/m^2) as compared to UP and epoxy. However, the results from HRR curves, Figure 4.5 (a), showed that although the PHRR of acrylic was lower than the others, it burned for longer time, hence showing relatively high THR and EHC of 109 MJ/m^2 and 22 MJ/kg respectively. The results for furan resin, with its high LOI value, show superior fire performance in comparison to the others. Furan resin ignited much later than any other resins at 84 s, and burned for a short time with very low PHRR of 613 kW/m^2 as seen in Figure 4.5 (a). Furan resin therefore shows very low THR (26 MJ/m^2) and EHC (10 MJ/kg) as compared to others, Table 4.6. Moreover, on comparing to others, furan resin produced much lower smoke, and significantly high char residue. This results, as expected due to the aromatic structure (see Figure 4.4), furan resin has high thermal stability, and on heating it decomposes with more char formation and yield less flammable products in comparison to others [8,9].

From all these flammability data, it can be clearly seen that among thermoset resin studied here furan resin has significantly lowest flammability than others, shown by the significantly high LOI; lowest PHRR, THR, EHC; and high char residue as compared to others.

4.3 Conclusions

The flammability results of different natural fibres were evaluated by LOI. On comparing the LOI values in both smouldering and flaming modes the flax and wool fibres had the highest fire resistant properties as compared to other fibres. However, the mechanical performance of a reinforcing fibre is the most important criterion for its selection in composite application [17], of the fibres studied here, flax and jute, with good mechanical properties, are more commonly used in composites [1,18]. Due to commercial interest, good mechanical properties, and satisfactory fire performance in comparison to other natural fibres [1,19], flax was selected for developing high performance natural fibre composites in this PhD.

For polymer matrix, the flammability results of different synthetic and bio based thermoplastic and thermoset polymers showed that the biopolymers of polylactic acid (PLA) and poly(furfuryl alcohol) (furan resin) were least flammable than others in their respective groups of polymers. And also, due to the environmentally friendly properties, which is one of the main advantages of

using natural fibre composites, PLA and furan resin are currently of interest for natural fibre composites as they are fully bio derived materials. Considering their high fire performance and environmental friendly properties, PLA and furan resin were chosen as thermoplastic and thermoset polymer matrices, respectively, for development of natural fibre composites in this PhD project. In the group of thermoplastic matrix, PP was also selected for further study. This was chosen despite its high flammability, because of commercial interest in this polymer. PP is the most popular polymer matrix currently used for natural fibre composites as it provides some other good properties to natural fibre composites such as processing suitability, chemical resistance, mechanical properties, and electrical properties [20].

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Chapter 5: Flame retardant composites from FR treated flax/PP and flax/PLA fabrics

The discussion in previous chapters revealed that low fire resistance of natural fibres is the main drawback in restricting their use for composites in applications where the fire regulations are stringent. Flame retardant (FR) treatments are therefore required to improve their fire resistance. In this chapter commingled flax/PP and flax/PLA fibres woven into fabric structures were selected for fabricating composite laminates and to render these flame retardant. Aqueous flame retardant solutions were applied on the fabrics by using a conventional pad-dry technique, commonly used in textile applications. Usually for textile finishes, fabrics are first scoured, which helps in improving the wet pickup. In the first part of this chapter the effect of fabric pre-treatment (scouring) on fire and mechanical performance of composites is discussed. The second part involves screening of flame retardants for flax/PP and flax/PLA composites in order to identify an effective flame retardant that can be applied on fabrics by using pad-dry technique. The third part quantifies the effect of flame retardant concentration on fire and mechanical performance of the derived composites in order to identify an optimised flame retardant formulation that significantly improves fire retardancy of each of flax/PP and flax/PLA laminates. In Part four, the effect of the pH of the FR solution is studied in order to find an optimised value for minimum effect on the fire and mechanical performance of the composites.

Part 1

5.1 The effect of fabric scouring (pre-treatment) on fire and mechanical performance of flax/PP and flax/PLA composites

For textile related applications flax fibres are usually scoured with sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3) or sodium phosphate (Na_3PO_4) solutions prior to other treatments in order to remove the impurity present in the fibres, resulting in improvement in the absorption of fibres for dyes and other finishes [1]. Scouring removes size, hemicelluloses, lignin, pectin, waxes etc from cellulosic fibres. In composites, however the presence of lignin, pectin could be advantageous as they are reported to have better thermal stabilities than cellulosic structures (*see Chapter 2*) [2,3]. Moreover, not much is known about the effect of scouring on physical, mechanical and flammability properties of the composites. Therefore, the aim of this section is to study the effect of scouring on the FR uptake levels of flax/PP and flax/PLA woven fabrics, and fire and mechanical performances of derived flame retardant composites from these fabrics. Mono-ammonium phosphate (AP), one of the commonly used flame retardants (FR) for cellulosic materials, has been chosen as a model flame retardant for this study.

5.1.1 Selection and optimisation of scouring solution for flax/PP and flax/PLA fabrics

In order to identify a suitable scouring agent and an optimised condition for scouring for each of commingled flax/PP and flax/PLA fabrics the fabrics were scoured with different alkaline solutions, NaOH, Na_2CO_3 and Na_3PO_4, by immersing the fabrics in the alkali solution of a particular concentration at a required temperature for a required period of time. The conditions used for scouring are given in Table 5.1, whereas the detailed method of scouring has been discussed in *Section 3.2.2.1* in *Chapter 3*. In order to analyse the effect of alkali solutions on different fibre types, flax fabric was also treated similar to flax/PP and flax/PLA fabrics. The masses of the fabrics before and after scouring treatment were recorded, from which percent mass loss of each fabric after scouring treatment was calculated and reported in Table 5.1.

Table 5.1: Mass losses of flax, flax/PP and flax/PLA fabrics after scouring

Sample	Scouring agent	Concentration (g/L)	Temp. (^oC)	Time (h)	Mass loss of the fabric (%)
Flax	NaOH	20	90	1	16.2
	Na_2CO_3	10	70	1	10.4
		10	70	2	11.9
	Na_3PO_4	10	50	1	10.1
		5	40	1	6.6
Flax/PP	NaOH	20	90	1	11.1
	Na_2CO_3	10	70	1	7.5
		10	70	2	7.7
	Na_3PO_4	10	50	1	7.0
Flax/PLA	NaOH	20	90	1	39.2
	Na_2CO_3	10	70	1	8.8
		10	70	2	10.9
	Na_3PO_4	10	50	1	5.5

The results show that 20 g/L NaOH is the most aggressive solution for scouring flax fabric as the percent mass loss is very high (16.2%), as compared to other solutions where the mass loss is about 10 - 12%. For flax/PLA a significant mass loss of 39.2% is observed after scouring with 20 g/L NaOH, which could be due to PLA dissolving in a strong alkaline solution. The ester group (-COO-) of PLA, similar to other aliphatic polyester, can hydrolyse with an alkali solution through saponification [4]. However, with Na_2CO_3 and Na_3PO_4 (weaker alkali agents) solutions the mass loss is less than with NaOH. In flax/PP fabrics the mass loss is less as compared to flax and flax/PLA fabrics, which is as expected due to the chemical resistance of PP.

As can be seen from the results in Table 5.1, with all scouring agents used the mass loss of all fabrics and in particular flax/PLA is more than expected if only size was removed. This could be due to hemicelluloses, lignin and pectin in flax fibres also being removed as the scouring agents could also react with these components and transform to water soluble salt products which are

easily removed from the fibres during the scouring process [1]. However, these components, in particular lignin, are useful for better fire performance of composites. Since the chemical structure of lignin molecules is three-dimensional and highly cross-linked aromatic structure, it contributes more to char formation, and hence is less flammable than cellulose [3]. Therefore, for good fire performance of composites these components should not be removed and only size needs to be removed. Scouring conditions need to be optimised to identify the minimum mass loss of fabrics that significantly improves FR uptake. Based on this criterion, Na_2CO_3 and Na_3PO_4 were selected for further study.

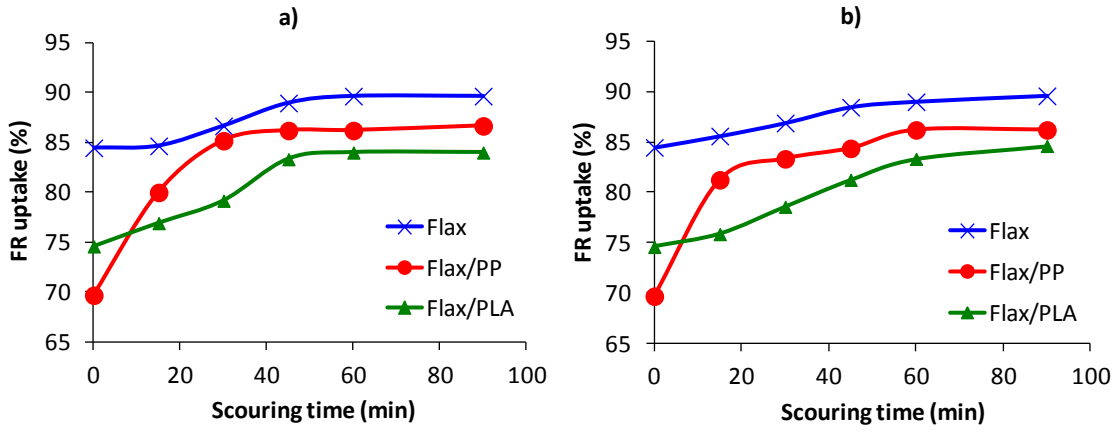

Figure 5.1: FR uptake of flax, flax/PP and flax/PLA fabrics after scouring with; a) Na_2CO_3 (10 g/L solution), b) Na_3PO_4 (10 g/L solution) for different times.

To optimise the scouring conditions for flame retardant treatment, flax, flax/PP and flax/PLA fabrics were scoured with 10 g/L solutions of Na_2CO_3 and Na_3PO_4 at 60°C for different times (15, 30, 45, 60 and 90 min), followed by treatment with AP flame retardant solution (20 wt-%) by using pad-dry technique (see *Section 3.2.2.2, Chapter 3*). The FR uptakes of these scoured fabrics were measured and are plotted as a function of scouring time in Figure 5.1. Non-scoured flax fabric, as expected, showed better FR pick-up (85%), as compared to non-scoured flax/PP (70%) and flax/PLA (75%) fabrics. On flax fabrics both Na_2CO_3 and Na_3PO_4 showed a very little effect of scouring up to 20 min. The FR uptake increased after 30 min, reaching a maximum of 90% after 60 min scouring. For flax/PP fabric, Na_2CO_3 increased the FR uptake from 70% to 87% in 30 min, which then remained stable up to 90 min. Similar trend was shown by Na_3PO_4. For flax/PLA, Na_2CO_3 significantly increased the FR uptake from 75% to 84% until 45 min, while Na_3PO_4 increased the FR uptake to same level after 60 min. Based on the results from this study, Na_2CO_3 (10 g/L solution) with 30 min scouring time was selected as an optimised condition to treat flax/PP and flax/PLA fabrics prior to treatment with the flame retardant.

5.1.2 Fire and mechanical performance of flax/PP and flax/PLA composite laminates

Eight layered flax/PP and flax/PLA composite laminates from non-scoured/scoured control and AP flame retarded flax/PP and flax/PLA fabrics were prepared., The optimised condition for scouring as identified above was used to treat the fabrics, while flame retardant treatment was padded on to the fabrics with 20 wt-% of AP solution. The details of the treated fabrics (mass losses after scouring and FR uptake) are given in Table 5.2. The fire and mechanical performances of these laminates were evaluated to study the effect of scouring on the properties of the FR flax/PP and flax/PLA composite laminates.

Table 5.2: Mass loss and percent FR content of flax/PP and flax/PLA fabric after scouring with Na_2CO_3 (10 g/L solution) and FR treatment with 20 wt-% of AP solution

Sample		Mass loss of fabric after scouring (%)	FR cont. on the fabric (%)
S-Flax/PP	(Scoured flax/PP fabric)	2.3 ±0.2	-
AP-Flax/PP	(FR treated flax/PP fabric)	-	11.3 ±2.4
S-AP Flax/PP	(Scoured and FR treated flax/PP fabric)	2.2 ±0.1	15.3 ±0.2
S-Flax/PLA	(Scoured flax/PLA fabric)	4.5 ±0.7	-
AP-Flax/PLA	(FR treated flax/PLA fabric)	-	12.3 ±0.7
S-AP Flax/PLA	(Scoured and FR treated flax/PLA fabric)	4.4 ±0.4	14.6 ±0.3

5.1.2.1 Fire performance of composites

To study the effect of scouring on flammability of FR treated flax/PP and flax/PLA laminates, the fire performance of the control and FR flax/PP and flax/PLA laminates prepared from non-scoured and scoured flax/PP and flax/PLA fabrics was studied by using UL-94 and cone calorimetric tests.

Flax/PP composites

The flax/PP laminates were tested for UL-94 standard test in both vertical and horizontal orientation and the results are given in Table 5.3. The control flax/PP failed the UL-94 vertical rating as the specimens were completely burnt up to the sample holder. The control flax/PP shows the burning rate of 166 mm/min in vertical and 21 mm/min in horizontal test.

Table 5.3: UL-94 results of control and AP treated flax reinforced PP composites

Sample	Horizontal flame spread			Vertical flame spread			V-rating
	B. Length (mm)	B. Time (s)	B. Rate (mm/min)	B. Length (mm)	B. Time (s)	B. Rate (mm/min)	
Flax/PP	100 ±1	295 ±32	21 ±2	100 ±1	36 ±2	166 ±8	Failed
S-Flax/PP	100 ±1	277 ±6	22 ±1	100 ±1	36 ±5	171 ±24	Failed
AP-Flax/PP*	-	-	-	100 ±1	93 ±4	65 ±3	Failed
S-AP Flax/PP*	-	-	-	100 ±1	96 ±1	63 ±1	Failed

* The flame went out before reaching the timing mark after removal of the burner

The treatment of flax/PP with mono-ammonium phosphate (AP) did not improve the UL-94 vertical rating of the AP-Flax/PP laminate, as the sample also burned completely. However, the vertical burning rate of flax/PP was significantly reduced to 65 mm/min (~ 60% reduction), and horizontal burning rate could not be calculated as the flame went out soon after removal of the burner, Table 5.3. The results in Table 5.3 show that the scouring process had a negative effect on the flammability of non-flame retarded flax/PP laminate as the rates of burning in vertical and horizontal orientations of the flax/PP laminate prepared from scoured fabric (S-Flax/PP) are higher than those of the non-scoured one, the results though are within the experimental error range, Table 5.3. The increase in the flammability of flax/PP after scouring process could be explained by the loss of lignin and pectin during scouring as these have better oxidation resistance and char formation than cellulosic structure [2,3]. On comparing the flammability of AP treated flax/PP laminates prepared from scoured and non-scoured fabrics, the scouring process showed a marginal effect. It can be seen that the vertical burning rate is slightly decreased from 65 mm/min in AP-Flax/PP to 63 mm/min in S-AP Flax/PP. The decrease in the flammability of S-AP Flax/PP could be due to the higher FR uptake by scoured fabric (Table 5.2), resulting in higher FR concentration in composite laminate produced from scoured fabric as compared to those of non-scoured samples.

The flammability of control and AP treated flax/PP laminates from scoured and non-scoured fabrics were also evaluated by using cone calorimetry at 35 kW/m^2. The heat release rate (HRR), rate of smoke release (RSR) and mass loss curves as function of time of these laminates are presented in Figure 5.2. The derived results from these curves in terms of time-to-ignition (TTI), flame-out-time, peak of heat release rate (PHRR), time to peak of heat release rate (T_{PHRR}), total heat released (THR) and effective heat of combustion (EHC) are presented in Table 5.4.

Table 5.4: Cone calorimetric results of control and AP treated flax/PP laminates at 35 kW/m^2

Sample	TTI	Peak 1		Peak 2		THR	EHC	TSR	Yield
	(s)	PHRR (kW/m^2)	T_{PHRR} (s)	PHRR (kW/m^2)	T_{PHRR} (s)	(MJ/m^2)	(MJ/kg)	(L)	(%)
Flax/PP	28 ±1	429 ±49	73 ±6	372 ±7	163 ±1	89 ±4	28 ±1	806 ±32	3.9 ±0.9
S-Flax/PP	26 ±3	477 ±13	72 ±1	400 ±2	104 ±6	92 ±6	28 ±1	848 ±22	3.3 ±0.8
AP-Flax/PP	28 ±1	255 ±6	66 ±1	199 ±5	311 ±7	81 ±1	25 ±1	667 ±21	13.3 ±0.9
S-AP Flax/PP	27 ±1	254 ±4	65 ±4	208 ±10	312 ±28	83 ±2	26 ±1	661 ±48	14.6 ±1.9

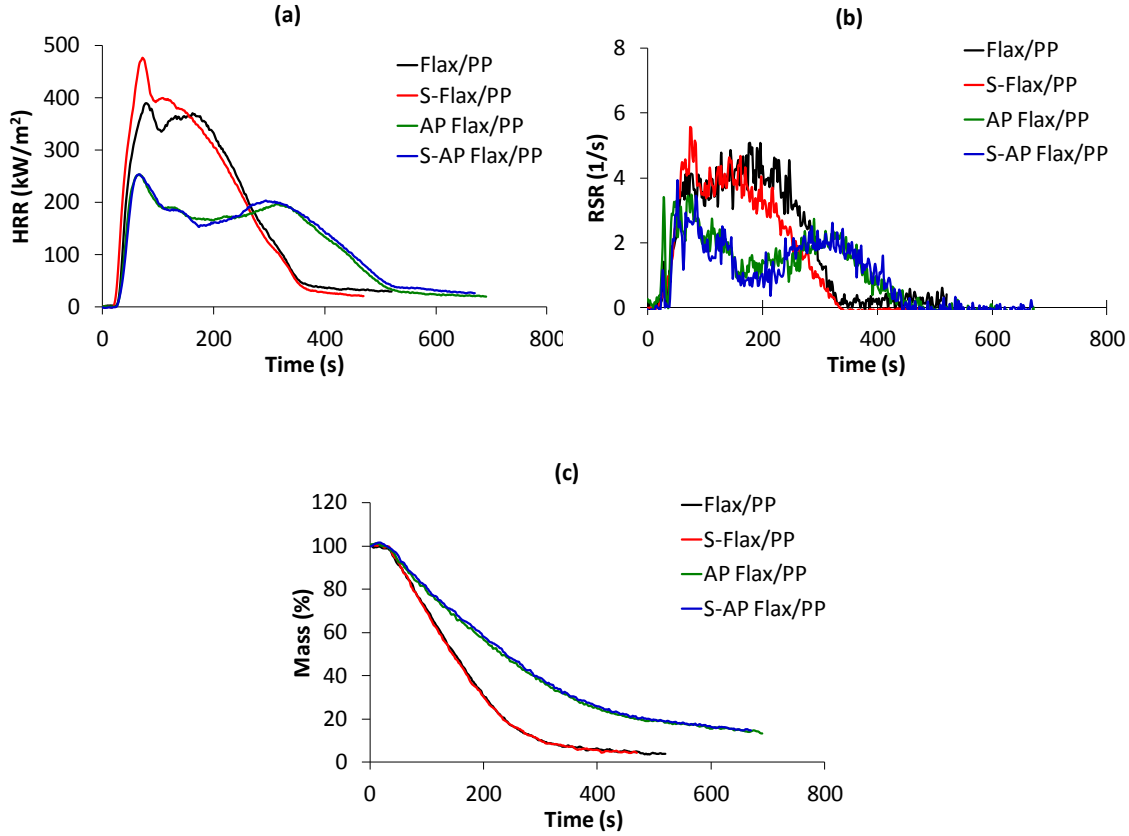

Figure 5.2: The cone calorimetric results of flax/PP laminates at 35 kW/m^2 heat flux: (a) Heat release rate (HRR), (b) smoke release rate (RSR), and (c) mass loss curves as function of time

Flax/PP laminate ignited at 28 s and showed two peaks of heat release rate (PHRR) of 429 and 372 kW/m^2 intensity at 73 s and 163 s, respectively, producing 89 MJ/m^2 of THR. These double peaked heat release rate behaviour of flax/PP laminate is a typical behaviour of a char forming material such as a cellulosic fibres reinforced composite. The first peak of heat release rate represents the burning of laminate after ignition. During which the flax fibres start charring. This charred layer could act as thermal barrier for the underlying polymer, slowing down its burning until the charred layer cracks and then the second peak appears [5]. Flax/PP produced total smoke release of 806 L, and 3.9% charred residue left at the end of the test. The mono-ammonium phosphate (AP) treated flax/PP laminate (11.3 wt-% in AP treated flax/PP fabric) had no effect on time-to-ignition (TTI) of the laminate (AP Flax/PP), but prolonged flame out time (FOT) from 344 s of control sample to 517 s. AP significantly reduced both PHRR values of Flax/PP. The first PHRR was reduced from 429 kW/m^2 of control sample to 255 kW/m^2 in AP-Flax/PP, indicating effectiveness of AP in reducing flammability. The second PHRR, which represents the effectiveness of char formed as a result of condensed phase activity of AP, was also decreased from 372 kW/m^2 in control flax/PP laminate to 199 kW/m^2 in AP-Flax/PP. THR (81 MJ/m^2) and EHC (25 MJ/kg) of AP-Flax/PP laminate were also reduced in comparison to the control sample (89 MJ/m^2 THR and 28 MJ/kg EHC). This could be explained by the FR activity of AP which generally works in condensed phase by promoting more char formation, which can act as a thermal barrier to inhibit further decomposition of the underlying polymer [6]. This condensed phase effect of AP is also supported by an improvement in char formation of

the sample, i.e. char yield increased from 4.3% in the control (flax/PP) to 13.3% in sample AP-Flax/PP. With the scouring process, the results of non-flame retarded flax/PP show that S-Flax/PP ignited at 26 s, and burned with two peaks of HRR of 477 and 400 kW/m^2, producing 92 MJ/m^2 THR. This indicates that scouring process slightly increased the flammability of non-flame retarded flax/PP, as seen from the reduction in the TTI; increase in PHRRs and THR in S-Flax/PP laminate as compared to the control flax/PP, Table 5.4. This is due to the removal of lignin and pectin during the scouring process, which can provide better char formation properties than cellulose [3]. The reduction in the oxidation resistance due to the loss of lignin and pectin can be also seen by slight decrease in the charred residue in S-Flax/PP (3.3%) compared to the control (3.9%). In case of the flame retarded flax/PP, as can be seen in Table 5.2 scouring helped to increase the FR uptake of flax/PP fabrics, hence the AP content in S-AP Flax/PP (15.3%) is higher than the sample from non-scoured fabrics (11.3% AP content in AP-Flax/PP). The S-AP Flax/PP was expected to show lower flammability when compared to AP-Flax/PP. However, this was not the case as can be seen from results in Table 5.4; scouring slightly reduced TTI, increased PHRRs, THR and EHC of FR treated flax/PP. These results though are within the experimental error range. This reduction in fire retardancy could be again due to removal of lignin and pectin from flax fibres during scouring process, increasing the overall cellulosic content of flax, which is more flammable [3].

Flax/PLA composites

The UL-94 results in Table 5.5 show that flax/PLA laminate failed the vertical rating test, and show vertical and horizontal rates of burning of 135 mm/min and 12 mm/min, respectively. This indicates the lower flammability of flax/PLA in comparison to the flax/PP as although flax/PLA also failed the vertical rating, it burned with lower rates of burning as compared to flax/PP (Table 5.3).

Table 5.5: UL-94 results of control and AP treated flax reinforced PLA composites

Sample	Horizontal flame spread			Vertical flame spread			Rating
	B. Length (mm)	B. Time (s)	B. Rate (mm/min)	B. Length (mm)	B. Time (s)	B. Rate (mm/min)	
Flax/PLA	100 ±1	497 ±21	12 ±1	100 ±1	45 ±3	135 ±7	Failed
S-Flax/PLA	100 ±1	462 ±6	13 ±1	100 ±1	42 ±3	143 ±10	Failed
AP-Flax/PLA*	-	-	-	-	-	-	V-0
S-AP Flax/PLA*	-	-	-	-	-	-	V-0

* Sample did not ignite, thus burning rate could not be calculated

The addition of AP in flax/PLA composite significantly reduced the flammability of flax/PLA and it can be seen that AP improved the vertical rating of flax/PLA from 'fail' in the control to V-0 rating in the AP-Flax/PLA, Table 5.5. The scouring increased the flammability of flax/PLA by increasing the rate of burning of flax/PLA in both vertical and horizontal orientations, Table 5.5. The effect is however not significant as the values are within the experimental error range. These results show the same trend as observed in flax/PP samples, and could be explained by

the loss of lignin and pectin, which provide better oxidation resistance and char formation than cellulosic structure [2,3], during the scouring process. The difference between AP treated flax/PLA from scoured and non-scoured fabrics could not be identified as both samples passed V-0 rating.

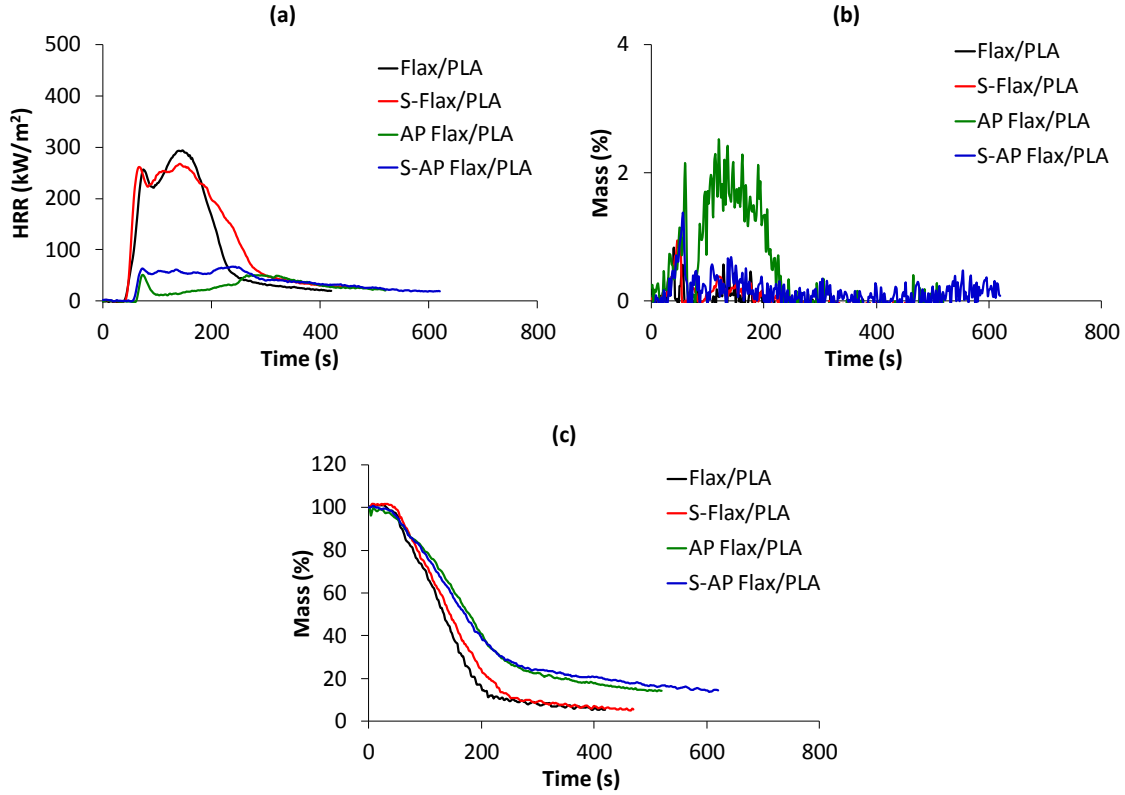

Figure 5.3: The cone calorimetric results of flax/PLA laminates at 35 kW/m^2 heat flux: (a) Heat release rate (HRR), (b) smoke release rate (RSR), and (c) mass loss curves as function of time

Table 5.6: Cone calorimetric results of control and AP treated flax/PLA composites at 35 kW/m^2

Sample	TTI	Peak 1		Peak 2		THR	EHC	TSR	Yield
	(s)	PHRR (kW/m^2)	T_{PHRR} (s)	PHRR (kW/m^2)	T_{PHRR} (s)	(MJ/m^2)	(MJ/kg)	(L)	(%)
Flax/PLA	49 ±2	266 ±34	69 ±7	287 ±10	142 ±3	48 ±3	12 ±1	16 ±4	4.1 ±1.0
S-Flax/PLA	48 ±4	267 ±20	67 ±4	270 ±35	142 ±3	54 ±2	12 ±1	25 ±9	3.7 ±2.5
AP-Flax/PLA	62 ±1	51 ±6	73 ±1	58 ±17	299 ±41	14 ±4	4 ±1	74 ±36	14.2 ±0.5
S-AP Flax/PLA	57 ±1	66 ±6	107 ±30	73 ±13	231 ±18	23 ±4	5 ±1	41 ±23	14.6 ±1.0

The cone calorimetric results of control and AP treated flax/PLA at 35 kW/m^2 external heat flux are graphically presented in Figure 5.3, and the derived data are given in Table 5.6. Flax/PLA laminate ignited at 49 s (21 s later than flax/PP), also showed two peaks of heat release, 266 kW/m^2 at 69 s and 287 kW/m^2 at 142 s, which are much lower than those of flax/PP (Table 5.4), hence producing lower THR (48 MJ/m^2) in comparison to flax/PP (89 MJ/m^2). These results indicate the lower flammability of flax/PLA in comparison to flax/PP composites, which is as expected due to the lower flammability of PLA as compared to PP (see *Chapter 4*). In AP flame

retarded composite (AP-Flax/PLA), TTI was delayed from 49 s to 62 s, and the PHRRs, THR and EHC decreased in comparison to the control. The PHRRs of flax/PLA were significantly reduced, the first PHRR to 51 kW/m^2 and the second to 58 kW/m^2, showing about 80% reduction of each peak in comparison to the control. THR was reduced from 48 MJ/m^2 in the control to 14 MJ/m^2 (71% reduction) and EHC was reduced from 12 MJ/kg to 4 MJ/kg (67% reduction). The AP also significantly improved the char formation of flax/PLA from 4.1% to 14.2% in AP-Flax/PLA. It can be seen from Table 5.6 that the efficiency of AP was more pronounced on flax/PLA composites. The difference of FR effectiveness of AP when used in flax/PP and flax/PLA can be explained by the presence of oxygen atoms in polymeric structure of PLA, (-COO-), providing better char formation properties of PLA during decomposition as compared to PP, hence PLA can be effectively flame retarded with the condensed phase flame retardant such AP [10,11]. The fire performance of flax/PLA can therefore be significantly improved compared to flax/PP, as both reinforcing fibres and polymer matrix are effectively flame retarded with AP. On comparing the cone calorimetric results of non-flame retarded flax/PLA laminates from scoured and non-scoured fabrics in Table 5.6, it can be seen that scouring did not affect the TTI and PHRRs but caused the sample to burn for longer time (Figure 5.3), hence producing higher THR in the S-Flax/PLA (54 MJ/m^2) in comparison to the control flax/PLA (48 MJ/m^2). The results of AP treated flax/PLA from the scoured fabrics (S-AP Flax/PLA) also show the same trend that the scouring increased the flammability of AP-Flax/PLA, by shorter TTI (57 s) of S-AP Flax/PLA in comparison to the AP-Flax/PLA (62 s), and respective higher PHRRs and THR values. The PHRRs were increased from 51 to 66 kW/m^2 for the first peak, and from 58 to 73 kW/m^2 in the second peak. The THR was significantly increased from 14 MJ/m^2 to 23 MJ/m^2 (~ 64% increment).

In summary, the UL-94 and cone calorimetric results of flax/PP and flax/PLA composites have shown that scouring of commingled flax/PP and flax/PLA fabrics prior to flame retardant treatment has a negative effect as it slightly increased the flammability of flame retarded flax/PP and flax/PLA composite laminates, seen from the slight increase in the rates of burning in the UL-94 test; the decrease in TTI and the increase in THR in cone calorimetry of the samples from the scoured fabrics in comparison to the non-scoured ones.

5.1.2.2 Mechanical performance of composites

The mechanical test results of the control and flame retardant flax/PP and flax/PLA composite laminates from scoured and non-scoured fabrics tested in tensile, flexural and impact modes are given in Table 5.7 and 5.8.

Flax/PP composites

The tensile modulus of control flax/PP was 6.6 GPa. With the AP treatment, the tensile modulus of flax/PP was reduced to 5.7 GPa in AP-Flax/PP. The tensile properties of composite laminates are reinforcement dependent [12], therefore the change in properties of reinforcing fibres also

affects the performance of their laminates. The reduction of tensile modulus in AP-Flax/PP could be explained by the fact that during laminate preparation, mono-ammonium phosphate (AP) could start decomposing (decomposition temperature is about 170 - 180^{o}C) producing phosphoric acid, which can cause hydrolysis of cellulose in flax fibres, leading to the reduction of the fibre strength and the tensile properties of the AP-Flax/PP in comparison to the control [13].

Table 5.7: Mechanical properties of scoured and flame retarded flax/PP composites

Sample	Tensile properties		Flexural Modulus	Impact Modulus
	Modulus (GPa)	Strength (MPa)	(GPa)	(GPa)
Flax/PP	6.6 ±0.2	79 ±1	8.2 ±0.5	11.0 ±0.1
S-Flax/PP	8.4 ±0.1	85 ±8	10.9 ±1.4	11.4 ±0.2
AP-Flax/PP	5.7 ±0.3	38 ±9	8.4 ±0.6	9.4 ±1.0
S-AP Flax/PP	6.2 ±0.9	50 ±8	8.8 ±1.5	9.5 ±0.2

Note: Fibre volume fractions in all flax/PP samples are ~ 40%

With the scouring process, the tensile modulus of the non-flame retarded flax/PP composites increased from 6.6 GPa in the control to 8.4 GPa in the S-Flax/PP (27% increase). The increase in tensile modulus of flax/PP laminate prepared from scoured fabrics could be explained by removal of size, hemicelluloses, lignin, pectin, waxes etc. in flax fibre during scouring process, leading to change in fine structure of cellulose and production of rough surface [14,15]. This physically improves interfacial bonding between fibre and matrix by giving rise to additional sites for mechanical interlocking, therefore promoting more polymer penetration at the interface [16-18]. The fibre-matrix interfacial adhesion plays an important role in mechanical performance of composites. The greater fibre-matrix adhesion gives better load-transfer between fibre reinforcement and polymer matrix resulting in greater mechanical performance [16-18]. In case of AP treated flax/PP, the results in Table 5.7 show that scouring also improved the tensile modulus of AP treated flax/PP, but the effect was less pronounced than observed in the non-flame retarded samples as the tensile modulus of AP-Flax/PP increased from 5.7 GPa to 6.2 GPa in S-AP Flax/PP (8% increase). This could be due to the scouring which also increased the AP content on the laminates (Table 5.2). Therefore the effect of scouring in increasing the tensile properties could be compensated by the higher degree of hydrolysis on flax fibres caused by the increased AP content, leading to lower efficiency in the AP treated flax/PP in comparison to the untreated one. A similar trend is seen in tensile strength (Table 5.7), which increased with scouring.

To support the discussion that scouring increased the tensile properties, particularly tensile strength, of the laminates by improving the fibre/matrix interfacial adhesion, the fractured surfaces after tensile tests of control and AP treated flax/PP laminates from scoured and non-scoured fabrics were observed by using scanning electron microscopy (SEM), Figure 5.4. As seen in Figure 5.4, the laminates from scoured fabric show better fibre-matrix adhesion in comparison to laminates from non-scoured fabric. Figure 5.4 (b) and (d) show that the fibre

breaking positions in control and flame retarded flax/PP laminate from scoured fabric are at similar level as the fractured surface of polymer matrix, which indicates a good adhesion between fibre and matrix [19,20]. Whereas, Figure 5.4 (a) and (c) for non-scoured sample show that the fibres have been pulled-out before breaking from the matrix, long fibres protruding through the fractured surface can be clearly seen. This shows that the scouring improved the fibre-matrix interfacial adhesion of composites resulting in improvement of mechanical properties as shown by increase of tensile properties (Table 5.7).

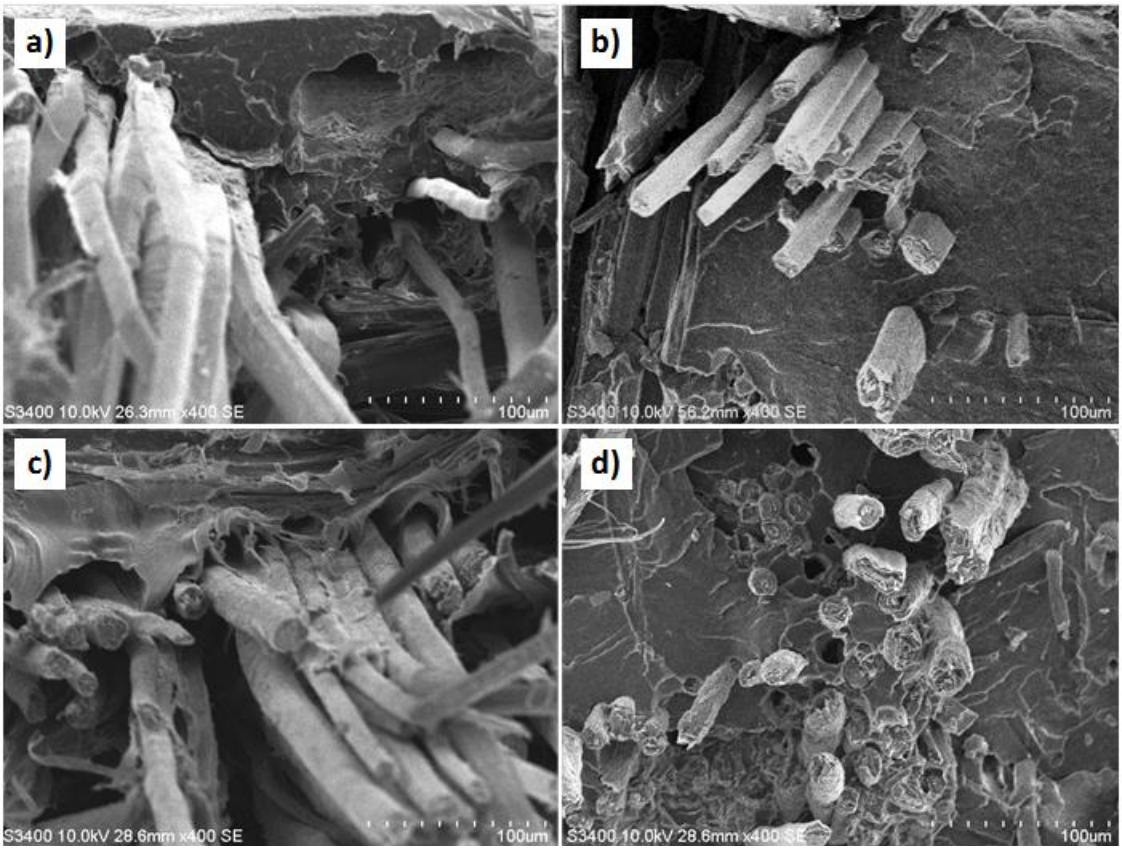

Figure 5.4: The SEM images of fracture surface of control and AP treated flax/PP laminates from scoured and non-scoured fabrics: (a) Flax/PP, (b) S-Flax/PP, (c) AP-Flax/PP, and (d) S-AP Flax/PP

In flexural mode, flax/PP shows the modulus of 8.2 GPa. With the addition of AP, the flexural modulus of flax/PP is slightly increased to 8.4 GPa in AP-Flax/PP. The effect of scouring on flexural properties is also similar to those observed in tensile results and it can be seen that the flexural moduli of control and AP treated flax/PP composites from the scoured fabrics are higher than the non-scoured ones The scouring increased flexural modulus of non-FR treated flax/PP from 8.2 GPa in control sample to 10.9 GPa in S-Flax/PP (33% increase), while for AP treated flax/PP it increased from 8.4 GPa to 8.8 GPa (4% increase). This also could be explained by the improvement in the fibre/matrix interfacial adhesion in scoured samples in comparison to the non-scoured ones as although the flexural properties of composites are polymer matrix dependent, the fibre/matrix interfacial adhesion plays an important role on the properties. The improvement in fibre/matrix adhesion can lead to better load-transfer between fibre reinforcement and polymer matrix, and hence results in higher flexural properties [16-18]. On

comparing the impact modulus of control and AP treated flax/PP from scoured and non-scoured fabrics, the results in Table 5.7 show similar trend as observed in flexural properties that scouring slightly improved the impact modulus of the laminates, i.e. the impact modulus of flax/PP is increased from 11.0 GPa in the control to 11.4 GPa, and for AP treated samples is increased from 9.4 GPa in AP-Flax/PP to 9.5 GPa in S-AP Flax/PP. This was as expected, as the impact properties of composites are also matrix dependent, and hence the similar trend as observed in flexural properties was expected to be seen.

Flax/PLA composites

The results in Table 5.8 show that flax/PLA laminate has tensile modulus of 10.2 GPa and tensile strength of 81 MPa. The addition of AP flame retardant treatment reduces the tensile modulus of flax/PLA to 4.1 GPa in AP-Flax/PLA (60% reduction), and significant reduction in tensile strength from 81 MPa to 14 MPa. The significant reduction in the tensile properties of flax/PLA, particularly when compared to flax/PP samples, can be explained by the fact that AP flame retardant not only produces the phosphoric acid to react with flax fibres during its partial decomposition, but also ammonia (NH_3), which can cause a degradation of PLA by hydrolysing the ester group (-COO-) in its polymeric structure, hence leading to a loss of mechanical properties of PLA and its composites [4].

Table 5.8: Mechanical properties of scoured and flame retarded flax/PLA composites

Sample	Tensile properties		Flexural Modulus	Impact Modulus
	Modulus (GPa)	Strength (MPa)	(GPa)	(GPa)
Flax/PLA	10.2 ±1.4	81 ±5	16.2 ±0.9	14.9 ±0.2
S-Flax/PLA	10.9 ±0.1	83 ±8	18.5 ±1.4	15.4 ±0.1
AP-Flax/PLA	4.1 ±1.5	14 ±4	4.7 ±0.8	1.6 ±0.2
S-AP Flax/PLA	4.5 ±0.9	14 ±9	4.9 ±2.8	1.9 ±0.8

Note: Fibre volume fractions in all flax/PLA samples are ~ 60%

On comparing the tensile results of non-flame retarded flax/PLA from scoured and non-scoured fabrics, the results show that scouring slightly improved the tensile properties of flax/PLA, as as shown by the increase in tensile modulus of flax/PLA from 10.2 GPa in the control to 10.9 GPa in S-Flax/PLA (7% increase). These demonstrate that the effect of scouring is less in flax/PLA laminates in comparison to that observed in flax/PP samples (33% increase). The lower efficiency of scouring in flax/PLA is due to the scouring agent used in this work was alkali chemical (i.e. Na_2CO_3), and can cause some hydrolysis of PLA, hence the improvement in mechanical properties of flax/PLA laminates is less. The effect of scouring is also seen in the results of AP treated flax/PLA in Table 5.8. Scouring increased the tensile modulus of AP-Flax/PLA from 4.1 GPa to 4.5 GPa in S-AP Flax/PLA.

In flexural mode, flax/PLA shows the modulus of 16.5 GPa (Table 5.8), and this is reduced with the addition of AP to 4.7 GPa in AP-Flax/PLA. This is due to the fact that flexural properties of

composites are polymer matrix dependent rather than fibre reinforcement [12], hence the loss in mechanical properties of PLA due to the reaction with AP leads to the reduction in the mechanical properties of the derived composites. On comparing the flexural results of flax/PLA laminates from scoured and non-scoured fabrics, the results show that scouring increased the flexural modulus of flax/PLA from 16.2 GPa in the control to 18.5 GPa in S-Flax/PLA. Similar observation is also seen in the AP treated flax/PLA samples, as the flexural modulus of AP-Flax/PLA is slightly increased from 4.7 GPa to 4.9 GPa in S-AP Flax/PLA. The effect of scouring on impact modulus is similar to that on flexural modulus. The control and flame retarded flax/PLA laminates from scoured fabrics also showed slightly higher impact modulus than non-scoured samples, Table 5.8.

From these mechanical results, it can be concluded that scouring improved the mechanical properties of flame retarded flax/PP and flax/PLA composites by improving the fibre/matrix interfacial adhesion of the composites. The improvement is however not significant, in particular in AP treated flax/PLA as the scouring agent (i.e. Na_2CO_3), being alkali, could also cause partial hydrolysis of PLA polymer.

5.1.3 Conclusions

The scouring process helped in increasing the FR uptake ability of flax/PP and flax/PLA fabrics therefore increasing the FR content on the laminates prepared from these fabrics. The FR treated flax/PP and flax/PLA composites from the scoured fabrics were therefore expected to show higher fire performance than the non-scoured ones. This however was not the case as the results show that the scouring process slightly increased flammability of the laminates, shown by increased PHRRs, THR and EHC from cone calorimetric results, which could be explained due to removal of hemicelluloses, lignin and pectin, which have higher thermal stability than cellulosic structure. However, scouring helped in increasing the mechanical properties, which can be explained due to change in the fine structure of cellulose, producing rough surface leading to interfacial bonding improvement by increasing additional sites of mechanical interlocking between fibre and matrix. The increase in mechanical properties with scouring process though is minimal. Since with scouring, the flame retardancy of the laminates is slightly reduced and the enhancement in mechanical properties is also marginal, it can be concluded that there is no advantage of using an extra process of scouring during flame retardant composite laminate preparation.

Part 2

5.2 Screening of flame retardants for flax/PP and flax/PLA composites

As discussed earlier, since the materials used for fabricating flax reinforced PP (Flax/PP) and PLA (Flax/PLA) in this chapter were as woven fabric structures of flax/PP and flax/PLA, the fabrics can be treated with flame retardants (FRs) by using conventional pad/dry technique for

textile applications. For this, the flame retardants should be water soluble. The limitation of most of the water soluble flame retardants used in textile application is their durability, but the durability is not an issue for composites because the reinforcing fibres are impregnated in the polymer matrix, which is relatively hydrophobic in the nature, therefore a leach out of FRs from the fibres would be minimal. In this work following commercially available water soluble FRs (Thor Specialities, UK) were selected based on their knowledge of FR efficiency in cellulosic materials: ammonium sulfamate (AS), ammonium bromide (AB), guanidine dihydrogen phosphate (GDP), guanylurea methylphosphonate (GUP), and a mixture of inorganic and organic phosphates (IP). These are mainly condensed phase FRs working to improve char formation of polymers, except ammonium bromide which works in the vapour phase to interfere with the combustion of polymers. The FRs selected here are not originally designed for high processing temperature application, i.e. melt-pressing for flax/PP and flax/PLA laminate preparation, therefore their thermal stability at composite processing temperature (180^{o}C) were investigated to identify their suitability to be used for producing flame retardant flax/PP and flax/PLA composites. The effect of the identified FRs on fire and mechanical performance of natural fibre reinforced composites from two different thermoplastic matrices, polypropylene (PP) and polylactic acid (PLA) was then studied in order to identify the most effective flame retardant for producing the high performance flame retardant flax/PP and flax/PLA laminates.

5.2.1 Thermal stability of flame retardants

The thermal stability of the FRs at the processing temperature of flax/PP and flax/PLA laminates (180^{o}C) was studied by using thermogravimetric analysis (TGA). Since these commercial FRs were supplied as the concentrated solutions, the solid powder of FRs were collected for thermal analysis by drying 10 g of concentrated flame retardant solutions at 50^{o}C for 24 h in an oven, and then allowing to cool down to room temperature in a desiccator. The thermal stability of these collected solid FRs was studied, heating from room temperature to 250^{o}C in TGA at 10^{o}C/min heating rate under flowing air atmosphere (100 ml/min). The TGA results are shown in Figure 5.5. The interpreted results in terms of onset of degradation temperature (T_{onset}) and percent mass residue at 180^{o}C are reported in Table 5.9.

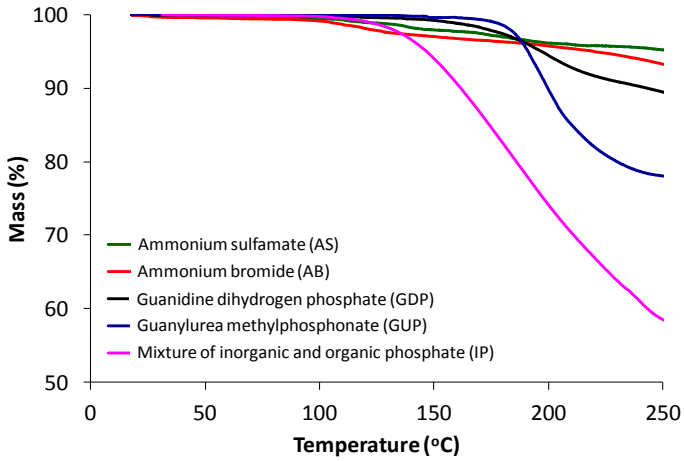

Figure 5.5: TGA curves of different flame retardants from room temperature to 250^{o}C in air

Table 5.9: Thermogravimetric results of flame retardants in air

Sample	Onset of decomposition Temperature (°C)	Residue at 180°C (wt-%)
Ammonium sulfamate (AS)	95	97.0
Ammonium bromide (AB)	99	96.3
Guanidine dihydrogen phosphate (GDP)	170	97.4
Guanylurea methylphosphonate (GUP)	183	98.6
Inorganic phosphate (IP)	137	82.5

Ammonium sulfamate (AS) starts losing mass at 95°C, but the maximum mass loss is 3% at 180°C. The TGA results in Table 5.9 show that ammonium bromide (AB) also shows similar behaviour, starts losing mass at 99°C, showing 3.7% mass loss at 180°C. These show that ammonium sulfamate (AS) and ammonium bromide (AB) start losing mass at lower temperature than the laminates processing temperature (180°C), their mass losses however are not significant. The phosphorus based FRs in this work show better thermal stability than both AS and AB flame retardants, except the mixture of inorganic and organic phosphate (IP). Guanidine dihydrogen phosphate (GDP) and guanylurea methylphosphonate (GUP) start losing mass at about 170 - 180°C, which is similar to the fabrication temperature of flax/PP and flax/PLA laminate. The mass loss up to 180°C for these FRs is 1 – 2% whereas, inorganic phosphate (IP) starts to decompose at 137°C, and then significant mass loss of 17% occurs by 180°C.

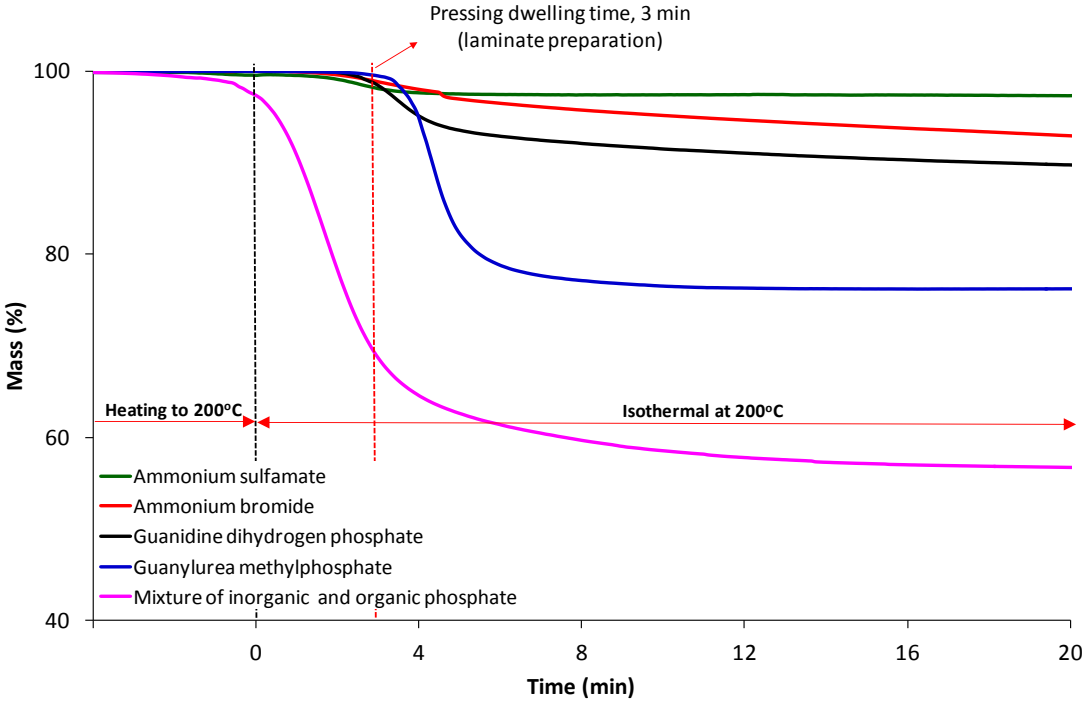

Figure 5.6: TGA curves of flame retardants in isothermal mode at 200°C in air

To confirm the suitability of these flame retardants, at 200°C, which is slightly higher temperature than the actual processing temperature used for flax/PP and flax/PLA composites, the flame retardants were heated in TGA to 200°C at heating rate of 25°C/min, and then isothermally held at this temperature for 20 min. This was to ensure that the FRs could sustain the high temperature during the laminate preparation. The mass loss results are given in Figure 5.6. The results show that ammonium sulfamate (AS) loses ~1% mass at the laminate processing temperature (200°C). On keeping the sample isothermally at 200°C, AS loses 3% mass in first 4 min, and then remains stable up to 20 min. Since the melt-pressing time for preparing flax/PP and flax/PLA laminates is 3 min (see *Section 3.2.5.1* in *Chapter 3*), this shows that AS could potentially be used for preparing the flame retardant flax/PP and flax/PLA composites as although it decomposes at 200°C but only small mass loss (< 4%) is observed. Ammonium bromide (AB) shows similar mass loss as observed in AS sample (~ 1%) at 200°C, and then gradually loses a further 2% after keeping isothermally for 3 min, hence demonstrating that AB can also be used for flax/PP and flax/PLA composites. Guanidine dihydrogen phosphate (GDP) shows no mass loss at 200°C. On keeping GDP at 200°C, there is no mass loss for 2 min, and then a gradual loss up to 2 and 8% at 3 and 20 min, respectively. The TGA results at 200°C of guanylurea methylphosphonate (GUP) in Figure 5.6 show that GUP shows no mass loss in first 3 min, and then gradually loses up to 22% at 6 min and then no further mass loss up to 20 min. On considering the mass loss results at 3 min of these GDP and GUP flame retardants, they are relatively thermally stable, and can be used for producing flame retardant flax/PP and flax/PLA composites. In contrast, IP shows low thermal stability as it starts decomposing before reaching 200°C, loses about 3% mass at 200°C, and then on keeping at 200°C 40% mass loss occurs within 4 min. Hence, it can be concluded from all TGA results discussed above that the majority of the selected FRs in this section, with the exception of the mixture of inorganic and organic phosphate (IP), could potentially be used to produce flame retardant flax/PP and flax/PLA laminates.

5.2.2 Flame retardant flax reinforced PP (Flax/PP) and PLA (Flax/PLA) composites

To study the effect of the potential flame retardants identified in above section on fire and mechanical performance of flax/PP and flax/PLA composites, the laminates were prepared from flax/PP and flax/PLA fabrics treated with aqueous solutions of these flame retardants. Since this work was a preliminary study to compare the efficiencies of different flame retardants, the FR content on the fabric was kept at approximately 10 wt-% in all samples, which achieves approximately 1% P content on the fabrics treated with phosphorus based flame retardants. To achieve the identified FR content, the fabrics were treated with 20 wt-% concentration of the FR solutions. The details of FR treated flax/PP and flax/PLA fabrics are given in Table 5.10.

Table 5.10: Details of flax/PP and flax/PLA fabrics treated with different flame retardant solutions

Sample	pH of applied FR solution	FR Cont (%)	P Cont. (%)	N Cont. (%)	S Cont. (%)	Br Cont. (%)
AS-Flax/PP	7.6	10.9 ±1.7	-	1.1 ±0.2	0.8 ±0.1	-
AB-Flax/PP	4.9	12.1 ±0.8	-	1.4 ±0.1	-	1.9 ±0.1
GDP-Flax/PP	5.4	10.6 ±0.9	1.0 ±0.1	1.1 ±0.1	-	-
GUP-Flax/PP	3.3	11.2 ±2.1	1.0 ±0.2	1.6 ±0.3	-	-
AS-Flax/PLA	7.6	10.1 ±1.1	-	1.0 ±0.1	0.8 ±0.1	-
AB-Flax/PLA	4.9	13.2 ±1.2	-	1.5 ±0.1	-	2.0 ±0.2
GDP-Flax/PLA	5.4	9.7 ±0.5	0.9 ±0.1	1.0 ±0.1	-	-
GUP-Flax/PLA	3.3	9.9 ±1.4	0.8 ±0.1	1.4 ±0.2	-	-

Note: The FR contents are the FR pickups on treated fabrics, calculated from the mass different of fabric before and after flame retardant treatment using Equation 3.2 given in *Chapter 3*. P, N, S and Br contents were calculated from the FR composition (information of FRs is given in *Chapter 3)* with respect to the FR pickup on fabrics.

The thermal stability, flammability and mechanical properties of these prepared FR flax/PP and flax/PLA laminates were investigated in order to identify the most effective flame retardant for flax/PP and flax/PLA composites.

5.2.2.1 Fire performance of composites

5.2.2.1.1 UL-94 test

The UL-94 results in terms of vertical rating and rate of burning in vertical and horizontal orientation are reported in Table 5.11.

Table 5.11: UL-94 results of FRs treated and untreated flax/PP and flax/PLA laminates

Sample	Horizontal			Vertical			
	B.Length (mm)	B.Time (s)	B.Rate (mm/min)	B.Length (mm)	B.Time (s)	B.Rate (mm/min)	V-rate
Flax/PP	100 ±1	150 ±13	19.3 ±1.3	100 ±1	44 ±1	141.7 ±18.0	Failed
AS-Flax/PP	100 ±1	290 ±35	10.2 ±2.5	100 ±1	88 ±2	68.6 ±1.7	Failed
AB-Flax/PP	16 ±3	493 ±6	2.4 ±1.2	100 ±1	81 ±6	73.0 ±5.3	Failed
GDP-Flax/PP	100 ±1	288 ±11	10.5 ±0.6	100 ±1	87 ±5	69.7 ±3.5	Failed
GUP-Flax/PP[1]	-	-	-	-	-	-	V-0
Flax/PLA	100 ±1	148 ±2	19.4 ±1.5	100 ±1	39 ±2	154.5 ±15.3	Failed
AS-Flax/PLA[2]	-	-	-	-	-	-	V-0
AB-Flax/PLA[2]	-	-	-	-	-	-	V-0
GDP-Flax/PLA[2]	-	-	-	-	-	-	V-0
GUP-Flax/PLA[2]	-	-	-	-	-	-	V-0

[1] The flame went out before reaching the timing mark after removal of the burner
[2] Sample did not ignite, hence the burning rate could not be calculated

In the vertical test, the control flax/PP and flax/PLA laminate failed the vertical rating, the specimens were completely burnt up to the sample holder indicating the low fire resistance of flax reinforced PP and PLA composites. The burning rate of flax/PP and flax/PLA was 141.7 and 154.5 mm/min, respectively. On addition of flame retardants in flax/PP composite laminates, all samples failed the vertical rating test, except for GUP-Flax/PP where V-0 rating could be achieved. However, all other FRs significantly reduced the rates of burning of the flax/PP laminates, at least by 50%, in horizontal and vertical orientation as can be seen in Table 5.11. The horizontal burning rate of flax/PP laminate is reduced from 19.3 mm/min to about 10 mm/min with the use of ammonium sulfamate (AS) and guanidine dihydrogen phosphate (GDP), while ammonium bromide (AB) and guanylurea methylphosphonate (GUP) show better results as the reduction is more than 50%. In GUP-Flax/PP laminate the flame went out before reaching the timing mark therefore the burning rate could not be calculated. From these results guanylurea methylphosphonate (GUP) was seen to be the most effective FR additive for improving the fire performance of flax/PP laminate.

The effect of these FRs was more pronounced when used in flax/PLA laminates, which could be due to PLA being more reactive towards flame retardants. All flame retardants improved the fire performance of flax/PLA significantly from 'fail' in the control sample to V-0 rating of UL-94 vertical test, Table 5.11. These results showed that UL-94 alone could not identify a very clear difference between the efficiency of each FRs on fire performance of the laminates, in particular flax/PLA. Therefore, the fire performance of the laminates was also evaluated by using cone calorimetry test at 35 kW/m^2 and the results are discussed in the following section.

5.2.2.1.2 Cone calorimetry

The cone calorimetric results of control and FR treated flax/PP and flax/PLA laminates are reported in terms of time-to-ignition (TTI), flame-out time (FOT), time to peak of heat release rate (T_{PHRR}), peak of heat release rate (PHRR), total heat released (THR), total smoke released (TSR), effective heat of combustion (EHC) and char residue, Table 5.12. The graphical presentation of heat release rate (HRR), rate of smoke release (RSR) and mass loss as a function of time are presented in Figure 5.7 and 5.8, respectively.

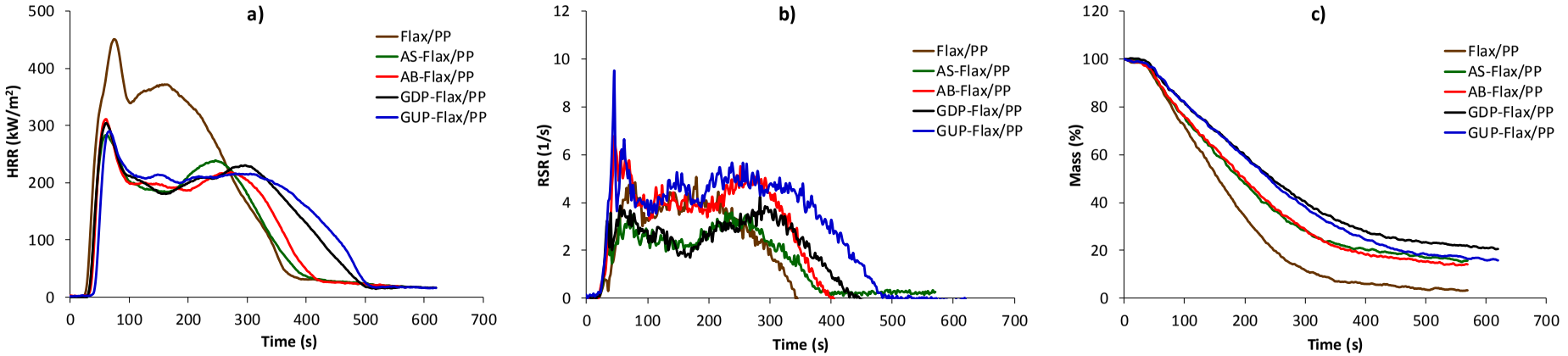

Figure 5.7: Cone calorimetric results of control and FR treated flax/PP composites at 35 kW/m^2: (a) HRR, (b) RSR, and (c) mass loss curves as a function of time

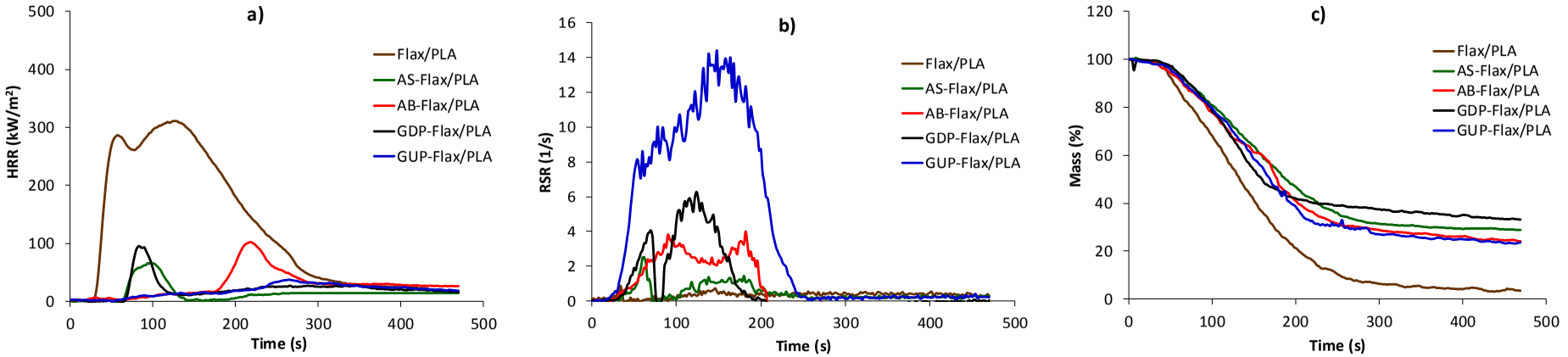

Figure 5.8: Cone calorimetric results of control and FR treated flax/PLA composites at 35 kW/m^2: (a) HRR, (b) RSR, and (c) mass loss curves as a function of time

Table 5.12: Cone calorimetric results of FRs contained flax/PP and flax/PLA laminates at 35 kW/m^2 external heat flux

Sample	TTI (s)	FOT (s)	Peak 1		Peak 2		THR (MJ/m^2)	EHC (MJ/kg)	TSR (L)	Yield (%)	Fire rating parameter (FIGRA, kW/m^2·s)
			T_{PHRR} (s)	PHRR (kW/m^2)	T_{PHRR} (s)	PHRR (kW/m^2)					
Flax/PP	31 ±2	363 ±5	75 ±3	452 ±8	160 ±12	374 ±8	98 ±3	27 ±1	970 ±59	3.3 ±0.9	6.0
AS-Flax/PP	36 ±3	403 ±14	61 ±1	284 ±8	244 ±5	239 ±5	70 ±3	24 ±1	870 ±145	15.8 ±1.0	4.7
AB-Flax/PP	38 ±3	400 ±22	61 ±1	312 ±7	271 ±2	219 ±10	72 ±3	22 ±1	1358 ±28	14.3 ±1.2	5.1
GDP-Flax/PP	36 ±3	502 ±12	61 ±1	305 ±7	297 ±9	231 ±9	83 ±2	25 ±1	1015 ±126	20.6 ±1.4	5.0
GUP-Flax/PP	46 ±2	500 ±9	67 ±5	297 ±16	244 ±49	221 ±10	87 ±2	23 ±1	1736 ±187	15.9 ±1.1	4.4
Flax/PLA	34 ±1	263 ±23	57 ±1	287 ±18	125 ±6	313 ±15	58 ±2	15 ±1	159 ±72	3.4 ±0.4	2.5
AS-Flax/PLA	65 ±3	224 ±139	126 ±17	74 ±12	-	-	15 ±12	3 ±1	179 ±20	29.0 ±4.6	0.6
AB-Flax/PLA	190 ±9	261 ±33	216 ±11	126 ±7	-	-	15 ±3	3 ±1	370 ±5	23.7 ±1.4	0.6
GDP-Flax/PLA	73 ±2	91 ±9	82 ±3	81 ±21	-	-	11 ±2	2 ±1	419 ±90	35.6 ±8.0	1.0
GUP-Flax/PLA	260 ±21	293 ±21	261 ±11	38 ±3	-	-	9 ±1	1 ±1	619 ±26	23.5 ±0.7	0.2

* FIGRA = PHRR divided by T_{PHRR} (kW/m^2.s) of the 1st Peak in all samples, except the control flax/PLA where the value was calculated from the 2nd peak as the value is higher than the first peak.

Flax/PP composites

The control flax/PP laminate ignited at 31 s and burned with double peaks of heat release rate of 452 and 374 kW/m^2 at 75 s and 160 s, respectively, producing 98 MJ/m^2 of THR. The results in Table 5.12 show that ammonium sulfamate (AS) delayed TTI of flax/PP from 31 s in the control to 36 s in AS-Flax/PP, and reduced both peaks of PHRR. The first PHRR is reduced from 452 kW/m^2 in the control to 284 kWm^2 in AS-Flax/PP, and the second from 374 kW/m^2 to 239 kW/m^2. These result in the lower THR in AS-Flax/PP (70 MJ/m^2), as compared to the control (98 MJ/m^2). AS-Flax/PP also shows lower EHC (24 MJ/kg) than the control, and produces higher char residue (15.8%) than the control (3.3%). In case of ammonium bromide, AB-Flax/PP ignited at 38 s, and burned with low PHRRs of 312 and 219 kW/m^2 in the first and second peak, respectively, producing a lower THR (72 MJ/m^2) than the control. The addition of AB also increased the charred residue of flax/PP from 3.3% in the control to 14.3% in AB-Flax/PP. These results indicate that AB show similar FR performance to improve fire retardancy of flax/PP as observed in AS sample, except that AB was less effective than AS in char formation (15.8% residue in AS-Flax/PP). This is as expected as AB generally works as a vapour phase flame retardant [7,21,22], hence the effect on char formation which is condensed phase activity is not observed. With the addition of guanidine dihydrogen phosphate (GDP), the results show that it delayed TTI of flax/PP from 31 s to 36 s in GDP-Flax/PP, and reduced the PHRRs to 305 kW/m^2 in the first peak, and 231 kW/m^2 in the second. GDP however caused the sample to burn for a longer time than the control (Figure 5.7 (a)), hence the reduction in the THR in GDP-Flax/PP (83 MJ/m^2) in comparison to the control (98 MJ/m^2) was not significant. GDP shows significant improvement in char formation as can be seen from the increase in charred residue from 3.3% in the control to 20.6% in GDP-Flax/PP, which is the highest value in comparison to other flax/PP samples, Table 5.12. The significant improvement in char formation of GDP-Flax/PP also showed an effect on time-to-second PHRR (297 s) as compared to the control flax/PP laminate (160 s). Since the second PHRR is related to a char formation of the flax fabric on the exposed surface of the samples, a higher char formation provides greater barrier properties to retard the pyrolysis of remaining materials [5]. In case of guanylurea methylphosphonate (GUP), the results showed that it prolonged TTI of flax/PP from 31 s to 46 s, which is the longest TTI value in comparison to others. GUP-Flax/PP also shows lower PHRRs than the control with the intensity of 297 kW/m^2 in the first peak and 221 kW/m^2 in the second, and resulting in the reduction in the THR of GUP-Flax/PP (87 MJ/m^2) as compared to the control (98 MJ/m^2). GUP also reduced the EHC of flax/PP from 27 MJ/kg to 23 MJ/kg in GUP-Flax/PP, and significantly increased the charred residue from 3.3% in the control to 15.9% in GUP-Flax/PP.

From these cone calorimetric results of control and FR treated flax/PP, it can be seen that all FRs significantly improved the fire performance of flax/PP composites as shown by the increase in TTI and char formation; reduction in PHRRs, THR and EHC. On comparing the efficiencies of different FRs, the difference between FRs was not significant, particularly the reductions in

PHRR and EHC, as all FR-flax/PP samples show almost similar values, Table 5.12. Hence to see the difference in the effect of FRs on the flammability of flax/PP more clearly, the fire growth rates (FIGRA) of these FR-flax/PP samples were also evaluated and reported in Table 5.12. The fire growth rate (FIGRA) = maximum quotient of $HRR(t)/T_{PHRR}$, which often equates to $PHRR/T_{PHRR}$ in a cone calorimeter [23], if the peak is sharp and the gradient is well defined, which is the case here. Materials with higher fire safety level should have lower FIGRA. On comparing the FIGRA results of control and FR treated flax/PP composites in Table 5.12, the FIGRA value of flax/PP (6.0 $kW/m^2.s$) is reduced with the addition of FRs, and GUP was seen to be the most effective FR for flax/PP composites as shown by the lowest FIGRA value in GUP-Flax/PP (4.4 $kW/m^2.s$), as compared to others, followed by AS-Flax/PP (4.7 $kW/m^2.s$), GDP-Flax/PP (5.0 $kW/m^2.s$), and AB-Flax/PP (5.1 $kW/m^2.s$), respectively. These values are in the same trend as observed in the UL-94 results where GUP-Flax/PP shows highest fire performance, Table 5.11.

Flax/PLA composites

Flax/PLA laminate ignited at 34 s, and burned with two PHRRs of 287 kW/m^2 at 57 s and 313 kW/m^2 at 125 s. The flax/PLA laminates produced THR of 58 MJ/m^2, and 3.4% charred residue. Flax/PLA shows EHC of 15 MJ/kg. On addition of ammonium sulfamate (AS), the flammability of flax/PLA was significantly reduced as can be seen that AS-Flax/PLA show TTI of 65 s which is much longer than the control (34 s), and burned with low intensity single peak of HRR of 74 kW/m^2 rather than two peaks as observed in the control flax/PLA, Figure 5.7 (b). In comparison to the control flax/PLA, AS-Flax/PLA also produced much lower THR (15 MJ/m^2), and higher charred residue (29.0%). The change in the burning behaviour of flax/PLA from two PHRRs in the control to single PHRR in AS-Flax/PLA could be explained by the significant increase in the char formation in AS-Flax/PLA as compared to the control. The char acts as an effective barrier protects the underlying materials from the heat and flaming zone, hence resulting in the change of burning behaviour of flax/PLA laminate from double PHHRs to single PHRR. This effect is also seen in all other FR treated flax/PLA samples, Figure 5.7 (b). In the presence of ammonium bromide (AB), AB-Flax/PLA shows significantly high TTI (190 s), single PHRR of 126 kW/m^2, and low THR of 15 MJ/m^2. AB-Flax/PLA also shows lower EHC (3 MJ/kg), and higher charred residue (23.7%) compared to the control, Table 5.12. The addition of GDP also improved the fire performance of flax/PLA as can be seen that GDP-Flax/PLA shows higher TTI of 73 s, and burned with much lower PHRR (81 kW/m^2). This therefore results in the lower THR (11 MJ/m^2) and EHC (2 MJ/kg) in GDP-Flax/PLA compared to the control, Table 5.12. GDP also significantly improved the char formation of flax/PLA from 3.4% in the control to 35.6% in GDP-Flax/PLA. In GUP-Flax/PLA, the GUP significantly delayed TTI of flax/PLA to 260 s, which is the highest value compared to other FR treated flax/PLA samples. In comparison to the control flax/PLA, GUP-Flax/PLA burned with significantly lower PHRR of 38 kW/m^2 at 261 s, producing 9 MJ/m^2 THR. GUP-Flax/PLA also shows significant reduction in the EHC (1 MJ/kg) compared to the control (15 MJ/kg). From these cone calorimetric results, it can be clearly seen that all FRs significantly improved the fire performance of flax/PLA, and the effect was more

pronounced than in flax/PP. And, on comparing the EHC of the FR treated flax/PLA samples, the results show that GUP was seen to be the most effective FR to flame retard flax/PLA composites, as shown by the highest reduction in the EHC in GUP-Flax/PLA compared to the control. The superior effectiveness of GUP in comparison to other FRs is also seen from the FIGRA results as GUP-Flax/PLA shows the lowest FHI value compared to others, Table 5.12.

5.2.2.2 Mechanical performance of composites

To study the effect of FRs on the mechanical performance of flax/PP and flax/PLA laminates, the laminates from control and FR treated fabrics have been evaluated for their mechanical properties in tensile, flexural and impact modes.

Flax/PP composites

The tensile results for flax/PP samples in terms of tensile modulus and tensile strength are reported in Table 5.13. Flax/PP shows 6.4 GPa of tensile modulus and 68 MPa of tensile strength. With the addition of FRs, these tensile properties of flax/PP are significantly decreased. For the tensile modulus, the results show that GUP-Flax/PP (3.4 GPa) shows the highest reduction in the tensile modulus, as compared to the control flax/PP, followed by AB-Flax/PP (4.7 GPa), GDP-Flax/PP (5.9 GPa), and AS-Flax/PP (6.1 GPa), respectively. While, the results in Table 5.13 show that the highest reduction in the tensile strength of FR treated flax/PP as compared to the control is observed in AB-Flax/PP, followed by AS-Flax/PP, GUP-Flax/PP, and GDP-Flax/PP, respectively.

Table 5.13: Mechanical properties of control and FRs treated flax/PP laminates

Sample	Tensile properties		Flexural Modulus (GPa)	Impact Modulus (GPa)
	Modulus (GPa)	Strength (MPa)		
Flax/PP	6.4 ±0.3	68 ±2	7.0 ±0.5	8.7 ±0.2
AS-Flax/PP	6.1 ±0.5 [-5%]	29 ±1 [-57%]	8.5 ±0.3 [+21%]	9.0 ±0.7 [+3%]
AB-Flax/PP	4.7 ±0.2 [-27%]	15 ±2 [-78%]	6.4 ±0.3 [-9%]	7.4 ±0.3 [-15%]
GDP-Flax/PP	5.9 ±0.2 [-8%]	41 ±3 [-40%]	7.2 ±0.6 [+3%]	8.0 ±0.3 [-8%]
GUP-Flax/PP	3.4 ±0.1 [-47%]	35 ±1 [-49%]	3.3 ±0.5 [-53%]	4.6 ±0.6 [-47%]

Note: Fibre volume fractions in all flax/PP samples are ~ 40%. Values in blankets represent percent change in the properties of FR treated composites with respect to the control

Since the tensile properties of composites are reinforcing fibre dependent, the properties of the fibres strongly affect the performance of the composites. The reduction in tensile properties of FR treated laminates can be explained by the change in properties of flax fibre after treatment with FR solutions. Since most of the FR solutions used in these were acidic solutions the cellulosic structure in flax fibres could be partially damaged by the acid, and may lead to a reduction in strength of flax fibre and a loss of tensile properties of their resulting laminates [13,24,25]. The reduction in the tensile properties, particularly the tensile modulus, of FR treated

flax/PP samples can be related to the pH values of the respective applied FR solution used for flame retardant fabrics (see Table 5.10). A generic trend can be seen that stronger acidic solution (i.e. lower pH value) causes higher reduction in the tensile properties of FR treated flax/PP laminates, as i.e. the solution of GUP with the pH of 3.3 causes the highest reduction, followed by AB (pH 4.9), GDP (pH 5.4), and AS (pH 7.6), respectively. In composites, the tensile properties are not only affected by reinforcing fibres but also by the interfacial adhesion between reinforcing fibre and polymer matrix [12]. The better fibre-matrix adhesion gives better load-transfer between fibre reinforcement and matrix resulting in a greater mechanical performance [18,26].

In order to study the fibre/matrix interfacial adhesion, the fractured surfaces of the control and FR treated flax/PP laminates were examined by using a scanning electron microscope (SEM), the micrographs are shown in Figure 5.9. The fractured surface of FR treated flax/PP samples, Figure 5.9 (b) – (e), show that the fibres were pulled out from the matrix, indicating the poor fibre/matrix interfacial adhesion [19,20]. Therefore, these show that FRs not only causes the reduction of the tensile properties of FR treated flax/PP laminates by a damage on flax fibres, but the presence of FRs also interferes with the adhesion between flax fibres and polypropylene.

Flexural and impact properties of control and FR treated flax/PP laminates are reported in term of modulus in Table 5.13. The flexural modulus of flax/PP laminate is 7.0 GPa. The flexural properties of FR treated flax/PP reported in Table 5.13 show that AS slightly improved the modulus, while GDP did not show an effect. AB and GUP caused reduction in flexural modulus as compared to that of the flax/PP, particularly GUP-flax/PP where the highest reduction (~ 50% reduction) was observed, Table 5.13. The flexural properties of composites are mainly related to the matrix performance, but they are also affected from the interfacial adhesion between fibre and polymeric matrix [12,16,27-30]. Hence, the loss in mechanical strength of flax fibres due to the acidity of the FR solutions also cuases the reduction in the flexural properties of the derived composites. While the increase in the flexural modulus in AS-Flax/PP (8.5 GPa) in comparison to the control (7.0 GPa) could be explained by the plasticising effect of AS, it has been reported that AS can provide not only flame retardant effect but also acts as a plasticiser to improve the melt flow of polymer during the laminate fabrication [31], which could possibly improve the properties of the laminates. In impact mode, the flax/PP shows the modulus of 8.7 GPa. With the addition of FRs, the results in Table 5.13 show similar trend as observed for flexural properties as most of FRs shows small effect on the impact modulus of flax/PP, except GUP-Flax/PP where there is a significant reduction in the impact modulus as compared to the control (~ 50% reduction). This was as expected, as the impact properties of composites are also matrix dependent, and hence the similar trend as observed in flexural properties was expected to be seen.

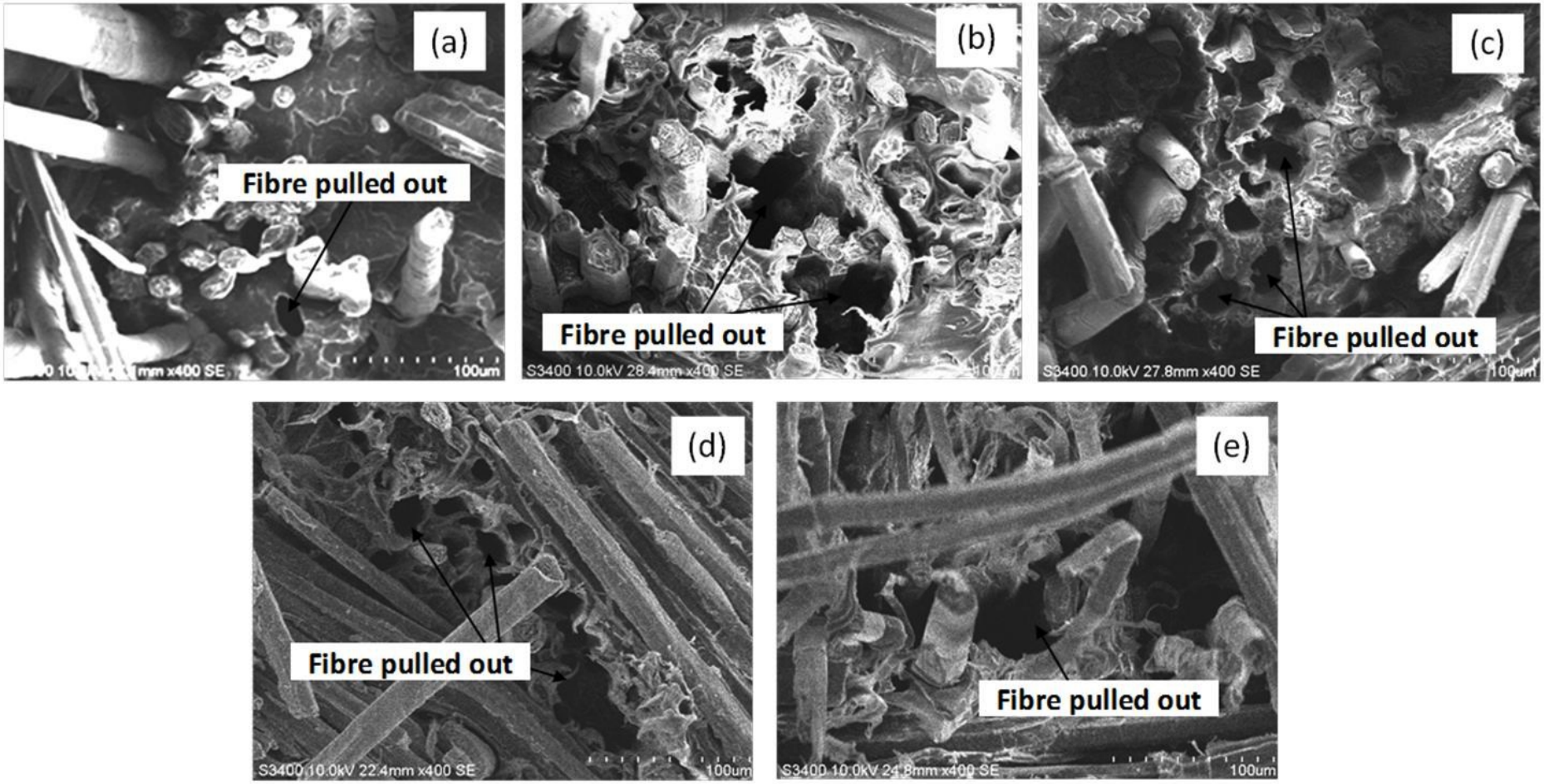

Figure 5.9: SEM images of the fracture surface of tensile tested specimens at 400X magnification; (a) Flax/PP, (b) AS-Flax/PP, (c) AB-Flax/PP, (d) GDP-Flax/PP, (e) GUP-Flax/PP

Flax/PLA composites

The mechanical properties of flax/PLA samples are reported in Table 5.14. In tensile mode, flax/PLA shows 9.0 GPa modulus and 86 MPa strength. On addition of FRs, tensile properties of flax/PLA were decreased, and the reduction was more severe than that observed in flax/PP samples. On comparing the reduction in tensile mudulii of FR treated flax/PLA samples, the results in Table 5.14 show that GUP caused the highest reduction in tensile modulus of flax/PLA from 9.0 GPa in the control to 5.0 GPa in GUP-Flax/PLA, followed by AB-Flax/PLA (6.4 GPa), GDP-Flax/PLA (7.1 GPa) and AS-Flax/PLA (7.6 GPa), respectively. These results show the same trend as observed in FR treated flax/PP sample, and hence could be also explained by the loss in mechanical strength of flax fibre caused by the acidity of the applied FR solutions where GUP solution shows the lowest pH (i.e. strong acid) in Table 5.10, hence resulting in the highest reduction in tensile properties of the derived composite in comparison to others.

Table 5.14: Mechanical properties of control and FRs treated flax/PLA laminates

Sample	Tensile properties		Flexural Modulus (GPa)	Impact Modulus (GPa)
	Modulus (GPa)	Strength (MPa)		
Flax/PLA	9.0 ±0.3	86 ±7	13.7 ±1.0	18.0 ±0.4
AS-Flax/PLA	7.6 ±1.1 [-16%]	14 ±1 [-84%]	9.8 ±0.4 [-29%]	15.7 ±0.4 [-13%]
AB-Flax/PLA	6.4 ±1.2 [-29%]	8 ±3 [-90%]	9.3 ±1.1 [-32%]	10.8 ±2.7 [-40%]
GDP-Flax/PLA	7.1 ±0.2 [-21%]	19 ±1 [-78%]	9.1 ±0.4 [-34%]	13.2 ±1.6 [-27%]
GUP-Flax/PLA	5.0 ±0.4 [-44%]	29 ±1 [-66%]	5.2 ±0.5 [-62%]	10.2 ±0.8 [-43%]

Note: Fibre volume fractions in all flax/PLA samples are ~ 60%. Values in blankets represent percent change in the properties of FR treated composites with respect to the control

On observing the fractured surface of these FR treated flax/PLA after tensile test, the results show contradictory effect as observed in flax/PP samples as can be seen from Figure 5.10 (b) – (e) that there were no clear evidence of poor interfacial adhesion or fibre pull-out in the FR treated flax/PLA samples. Therefore, the reduction of tensile properties of FR treated flax/PLA laminates, which is more severe than those flax/PP samples, is possibly due to the chemical reaction between FRs and PLA. Since PLA contains ester functional groups (-COO-) in its polymeric structure, the ester group makes PLA reactive to chemicals and may undergo hydrolysis [32,33]. Therefore, as a result of partial decomposition of the selected FRs in this work which are nitrogen based chemicals at the laminate processing temperature, Table 5.9, alkali species, i.e. ammonia, guanidine and guanylurea, can be released and subsequently cause a degradation of PLA by hydrolysing the ester groups in PLA structure, and hence results in a drop of mechanical properties of PLA and its composites [4].

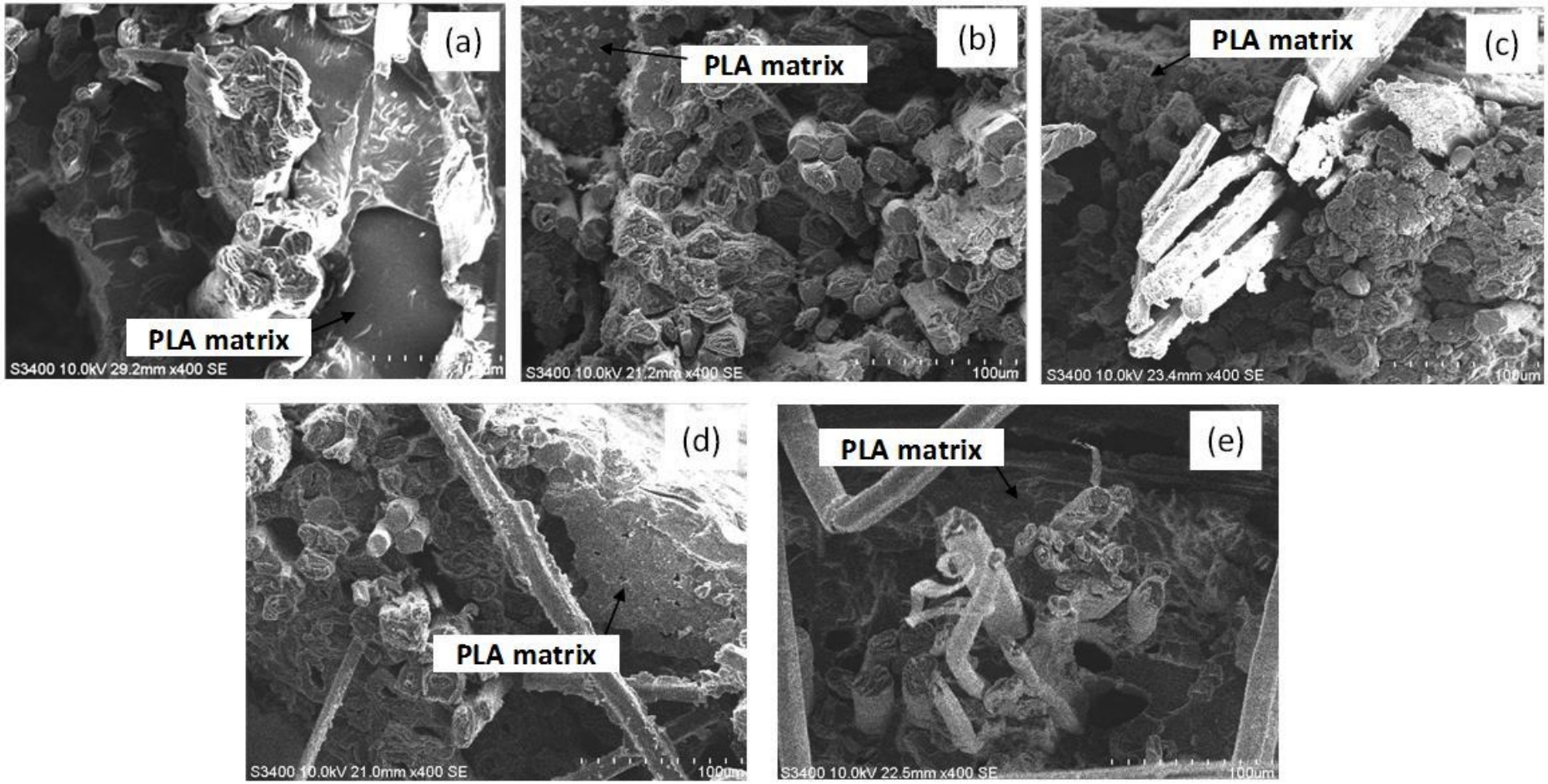

Figure 5.10: SEM images of the fracture surface of tensile tested specimens at 400X magnification; (a) Flax/PLA, (b) AS-Flax/PLA, (c) AB-Flax/PLA, (d) GDP-Flax/PLA, (e) GUP-Flax/PLA

The change in mechanical properties of PLA due to the degradation can be seen from the fractured surface of PLA in the laminates, Figure 5.10, as the breaking behaviour is changed with the FRs. The PLA matrix in the control flax/PLA laminate was cracked with a smooth fractured surface, suggesting being a rigid and brittle failure, whereas the PLA matrix in FRs treated flax/PLA broke in different manner with the production of rough fracture surface. In flexural test, the results in Table 5.14 show that the flexural modulus of flax/PLA (13.7 GPa) was reduced with all FRs. The highest reduction was seen in GUP-Flax/PLA (5.2 GPa, 62% reduction), followed by AB-Flax/PLA (9.1 GPa), GDP-Flax/PLA (9.3 GPa) and AS-Flax/PLA (9.8 GPa), respectively. These results also show that the effect of FRs on the reduction in flexural properties of flax/PLA was more severe than in flax/PP, especially with the ammonium sulfamate as it also caused reduction in flax/PLA but not in flax/PP. This is due to the FRs not only caused the reduction in mechanical strength of flax fibres, but also the PLA matrix due to the hydrolysis caused by liberated alkali from partial decomposition of FRs, hence resulting in the severe reduction in the flexural properties of flax/PLA. The impact results of FR treated flax/PLA laminates also show the same trend as the flexural properties, the former also being matrix dependent properties. The impact modulus of flax/PLA (18.0 GPa) is significantly decreased with GUP flame retardant to 10.2 GPa in GUP-Flax/PLA. This is followed by AB-Flax/PLA with the impact modulus of 10.8 GPa, GDP-Flax/PLA (13.2 GPa) and AS-Flax/PLA (15.7 GPa), respectively.

5.2.2.3 Thermal decomposition of composites

To have better understanding of the effect of FRs on flax/PP and flax/PLA composites, especially on the fire performance of the composites, the thermal stability of control and FR treated flax/PP and flax/PLA composites were studied under air atmosphere from room temperature up to 700^{o}C. The TGA curves of all samples, and detailed derivative thermogravimetric analysis (DTG) and differential temperature analysis (DTA) curves of one exemplar sample are presented in Figure 5.11 and 5.12. The analyses of all results are presented in Table 5.15 and 5.16.

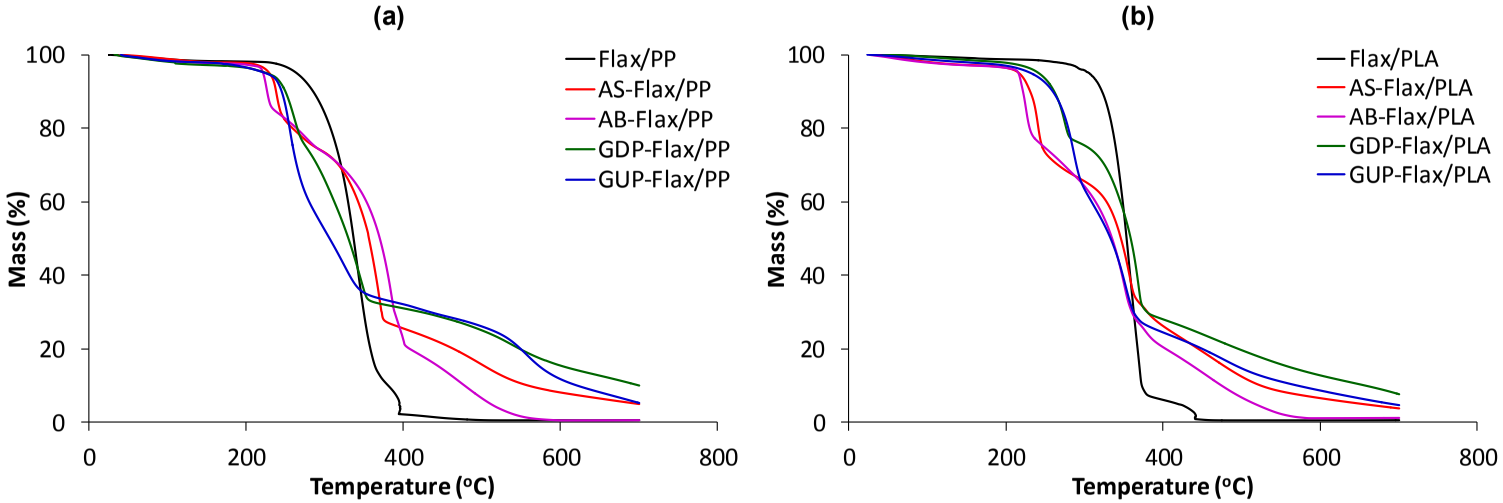

Figure 5.11: TGA curves of control and FR treated (a) flax/PP and (b) flax/PLA composites in air

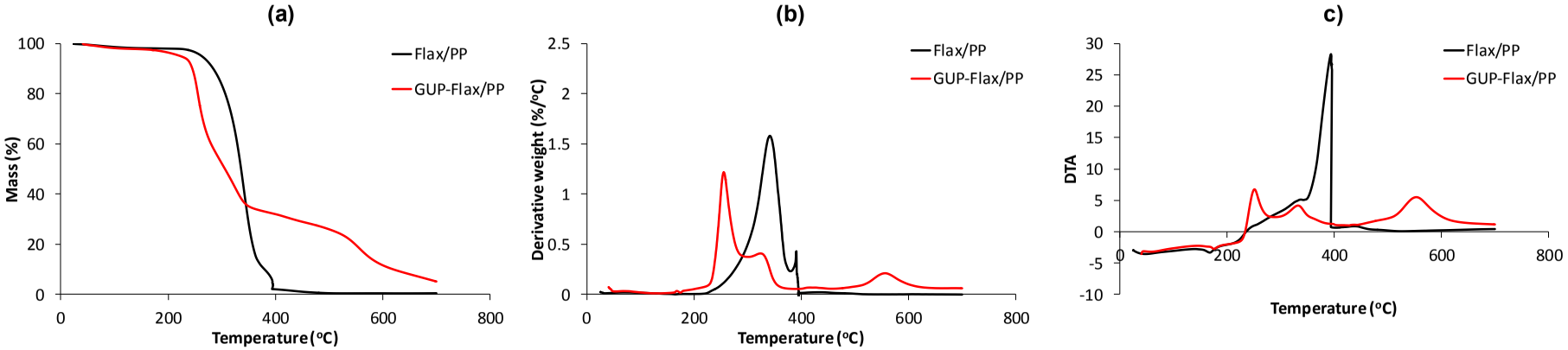

Figure 5.12: TGA (a), DTG (b) and DTA (c) curves of control and GUP treated flax/PP (GUP-Flax/PP) composites in air

Table 5.15: TGA, DTG and DTA results of control and FR treated flax/PP composites in air

Sample	Decomposition						Oxidation of char			Residue at 700°C (%)	DTA peaks	
	1st Mass loss step			2nd Mass loss step								
	Temp range (°C)	Mass loss (%)	DTG max (°C)	Temp range (°C)	Mass loss (%)	DTG max (°C)	Temp range (°C)	Mass loss (%)	DTG max (°C)		Melting (°C)	Decomposition (°C)
Flax/PP	219* - 380	87.8	341	-	-	-	380 - 395	10.0	391	0.3	168 (En)	394,437 (Ex)
AS-Flax/PP	194* - 293	23.8	239	293 - 385	48.6	368	385 - 589	22.4	497 (s)	2.9	166 (En)	238,372,488 (Ex)
AB-Flax/PP	209* - 241	13.1	225	241 - 412	64.2	384	412 - 601	18.7	471 (s)	0.8	166 (En)	223,401,482 (Ex)
GDP-Flax/PP	200* - 276	22.2	261	276 - 376	43.0	344	376 - 633	26.1	537 (s)	5.1	166 (En)	263,350,536 (Ex)
GUP-Flax/PP	186* - 299	44.4	256	299 - 381	19.8	324	381 - 630	29.9	557 (s)	3.1	166 (En)	251,333,554 (Ex)

Note: * = Onset of decomposition temperature. There is small mass loss (~ 3%) from room temperature (RT) to the onset of decomposition temperature, corresponding to the volatilisation of moisture in the samples. (s) represents small peak. (En) and (Ex) represent endothermic and exothermic DTA peak, respectively.

Table 5.16: TGA, DTG and DTA results of control and FR treated flax/PLA composites in air

Sample	Decomposition						Oxidation of char			Residue at 700°C (%)	DTA peaks	
	1st Mass loss step			2nd Mass loss step								
	Temp range (°C)	Mass loss (%)	DTG max (°C)	Temp range (°C)	Mass loss (%)	DTG max (°C)	Temp range (°C)	Mass loss (%)	DTG max (°C)		Melting (°C)	Decomposition (°C)
Flax/PLA	252* - 388	91.1	358	-	-	-	388 - 440	6.3	436	0.8	169 (En)	344 (En); 379,441 (Ex)
AS-Flax/PLA	201* - 290	29.6	240	290 - 412	40.6	356	412 - 565	22.2	463 (s)	3.9	160 (En)	240 (En); 376,488 (Ex)
AB-Flax/PLA	206* - 246	21.0	225	246 - 405	55.4	349	405 - 590	18.5	458 (s)	1.1	156 (En)	228 (En); 372,462 (Ex)
GDP-Flax/PLA	199* - 290	21.5	273	290 - 392	47.7	366	392 - 614	20.9	467 (s)	7.6	164 (En)	279,379 (Ex)
GUP-Flax/PLA	192* - 310	36.2	286	310 - 393	35.1	351	393 - 623	21.3	475 (s)	4.6	157 (En)	289,368,468 (Ex)

Note: * = Onset of decomposition temperature. There is small mass loss (~ 3%) from room temperature (RT) to the onset of decomposition temperature, corresponding to the volatilisation of moisture in the samples. (s) represents small peak. (En) and (Ex) represent endothermic and exothermic DTA peak, respectively.

Flax/PP composites

The TGA results in Table 5.15 show that flax/PP composite decomposes with two step thermal decomposition. The first step occurs between 219 – 380^{o}C losing 87.8% mass loss with the DTG max at 341^{o}C, representing the decomposition of flax/PP composite. In the second mass loss step, flax/PP shows 10.0% mass loss between 380 - 395^{o}C, and DTG max at 391^{o}C. This second step is accompanied by the exothermic DTA peak at 394^{o}C and 437^{o}C, representing oxidation of char formed in the first decomposition step. Flax/PP left almost no charred residue (0.3%) at 700^{o}C.

The addition of ammonium sulfamate (AS) changed the thermal decomposition of flax/PP from two to three mass loss steps. The additional decomposition step occurs at relatively low temperature as compared to the decomposition of control flax/PP, between 194 – 293^{o}C, which could be due to the low thermal stability of AS flame retardant as discussed in *Section 5.2.1*. This is followed by the second mass loss step taking place in the temperature range of 293 – 385^{o}C with 48.6% mass loss. This two steps decomposition is corroborated by two exothermic DTA peak at 238 and 372^{o}C. Then, the oxidation of the char formed in the previous stage occurs between 385 - 589^{o}C leaving higher charred residue of 2.9% at 700^{o}C as compared to the control (0.3%). During the decomposition in the first step of AS-Flax/PP ammonia and sulphuric acid could be produced from the decomposition of AS (Eq. 1), the latter could then provide the condensed phase FR activity by reacting with composite's components through a sulphation reaction, particularly with flax fibre. As a result of the sulphation reaction, the sulphate ester is formed in the sample, and influences the decomposition of the flax to promote more char formation at the expense of flammable volatiles [3,21,34-36], as can be seen from the comparatively low mass loss in second steps of AS-Flax/PP, and the increase in the charred residue in AS-Flax/PP in comparison to the control, Table 5.15. Hence, due to less flammable products being produced AS-Flax/PP therefore exhibits lower flammability than the control flax/PP as discussed in *Section 5.2.2.1*.

$$NH_4(SO_3NH_2) \xrightarrow{\triangle} 2NH_3 + H_2SO_4 \quad (1)$$

The ammonium bromide treated flax/PP (AB-Flax/PP) also shows three mass loss stages similar to that observed in AS-Flax/PP. The first step occurs at relatively low temperature (209 - 241^{o}C) as compared to the control which is due to the low thermal stability of AB flame retardant as it has similar thermal stability as ammonium sulfamate (see Table 5.9). In the second mass loss step, AB-Flax/PP shows mass loss of 64.2% between 241 – 412^{o}C, followed by the char oxidation stage between 412 – 601^{o}C producing 0.8% residue at the end. This shows that AB also improved the thermal stability of flax/PP, but the effect was less than that observed in AS-Flax/PP especially for char formation. This is due to AB flame retardant generally works in the vapour phase rather than condensed phase as in case of ammonium sulfamate, hence the improvement in the solid phase of the AB-Flax/PP was lower than AS-Flax/PP. As in this case hydrogen bromide (HBr), produced from decomposition of AB (Eq. 2) could work both in the

condensed and vapour phases by working as a Lewis acid, it reduces the decomposition, as can be seen from the comparatively low mass loss and the shift of DTG max to higher temperature in the second mass loss step, which is main decomposition of AB-Flax/PP, as compared to the control flax/PP. This therefore results in the decrease in flammability of AB-Flax/PP as can be seen from the increase in TTI; reduction in PHRR, THR and EHC in AB-Flax/PP as compared to the control, Table 5.12.

$$NH_4Br \xrightarrow{\triangle} NH_3 + HBr \qquad (2)$$

Guanidine dihydrogen phosphate treated flax/PP (GDP-Flax/PP) show the first mass loss step between 200 - 276^{o}C with the mass loss of 22.2%, representing the early decomposition of GDP flame retardant and its reactivity with flax. This is followed by the second mass loss step occurring in the range of 276 – 376^{o}C with 43.0% mass loss, and the oxidation of char formed in the previous stage between 376 – 633^{o}C giving 5.1% residue at the end. These results show that GDP improved the thermal stability of flax/PP to decompose with more char formation as can be seen from the significant increase in residue in GDP-Flax/PP as compared to the control (0.3%). This can be explained by the FR activity of GDP which is dominant in the condensed phase as the phosphoric acid produced from the decomposition of GDP in the first step could react with the composite's component through phosphorylation [36,37], accompanied by the exothermic DTA peak max at 263^{o}C, to form phosphate ester which influence the decomposition pathway of the sample to yield more char and less flammable product [21,34]. This therefore results in the higher thermal stability results of GDP-Flax/PP (Table 5.15), and lower flammability of GDP-Flax/PP in comparison to the control (Table 5.12). Moreover, in comparison to other FR treated flax/PP the char formation in GDP-Flax/PP is also higher than others, i.e. 5.1%. This is due to the synergistic effect between phosphorus (P) and nitrogen (N) elements in GDP flame retardant in the condense phase of the sample. With the presence of N compound, the phosphoric acid produced from decomposition of GDP, can form the P-N bonded intermediates which are more reactive phosphorylating agent, hence leading to the enhancement in the efficiency in the condensed phase of GDP to improve char formation of flax/PP composite [7,11,22,38,39]. In case of guanylurea methylphosphonate (GUP), GUP-Flax/PP also decomposes with three mass loss steps similar to others FR treated flax/PP composites. The first step is between 186 – 299^{o}C showing mass loss of 44.4% with the DTG max at 256^{o}C. The mass loss in this step is related to the decomposition of GDP at relatively low temperature due to its relatively low thermal stability (see *Section 5.2.1*) and reacts with flax and may be PP. The composite further decomposes between 299 – 381^{o}C with the DTG max at 324^{o}C in the second step, accompanied by the exothermic DTA peak at 333^{o}C, representing the main decomposition step. This is then followed by the char oxidation of the product from the decomposition in the previous stage giving 3.1% charred residue at the end. GUP similar to GDP produces phosphoric acid, which could then react with flax through phosphorylation reaction, resulting in the formation of phosphate ester in the composite which can influence the decomposition of the sample to yield less flammable product and more char formation. This therefore leads to the reduction in flammability of GUP-Flax/PP as compared to the control.

Flax/PLA composites

The TGA results in Figure 5.11 and Table 5.16 show that Flax/PLA composite decomposes with two mass loss steps similar to that seen in untreated flax/PP. The first step occurs between 252 – 388^{o}C, showing 91.1% mass loss and DTG max at 358^{o}C. This is accompanied by an endothermic DTA peak at 344^{o}C overlapped by an exothermic peak at 379^{o}C, representing the decomposition of flax/PLA. The flax/PLA then further loses mass up to 440^{o}C with the DTG max at 436^{o}C, producing 0.8% residue at the end. The second mass loss is corroborated by the exothermic DTA peak max at 441^{o}C, representing the thermal oxidation of the residue formed in the first mass loss step. On addition of ammonium sulfamate, AS-Flax/PLA decomposes with three mass loss steps similar to that observed in other FR treated flax/PP samples. The first step occurs in the relatively low temperature range (201 – 290^{o}C), which was expected due to the low thermal stability of AS flame retardant similar to that observed in AS-Flax/PP sample. This is followed by second mass loss step between 290 – 412^{o}C, showing 40.6% mass loss and 356^{o}C DTG max. And then, the char oxidation step from 412^{o}C to 565^{o}C, producing 3.9% charred residue. Figure 5.11 shows that AS improved the thermal stability of flax/PLA mainly by increasing the char formation of flax/PLA. This effect is similar to that seen in AS-Flax/PP sample, the action of AS on flax/PLA can be explained due to the sulphuric acid produced during the decomposition step of AS can react with flax to produce more char at the expense of the volatile products. This therefore leads to the reduction in flammability of AS-Flax/PLA compared to the control. Moreover, on comparing to the AS-Flax/PP the results show that AS is more effective in flax/PLA as can be seen by the higher charred residue in AS-Flax/PLA (3.9%) compared to AS-Flax/PP sample (2.9%). This could be due to the difference in polymer matrix between these two composite systems. In comparison to PP which generally decompose with no char residue, PLA contains oxygen element in its chemical structure providing better char formation properties during decomposition [10,11,40], hence PLA can be more effectively flame retarded with the condensed phase flame retardant such AS. This therefore also results in the higher FR performance of AS in flax/PLA compared to that in flax/PP composites as discussed in *Section 5.2.2.1*. With the addition of ammonium bromide, AB-Flax/PLA also shows three mass loss steps. The mass loss in two steps between 206 - 246^{o}C and 246 - 405^{o}C show that AB reduced the decomposition of flax/PLA composite, as when compared to the mass loss during the decomposition of PLA (91.1%) the sum of mass loss in these two steps (76.4%) is lower. The results in the last mass loss step show that the product from the decomposition in previous stages is oxidised, producing 1.1% charred residue at 700^{o}C. In comparison to other FR-Flax/PLA samples, this improvement in char formation of AB-Flax/PLA is less than others (Table 5.16), which was as expected due to AB working in the vapour phase as discussed earlier.

With guanidine dihydrogen phosphate (GDP), GDP-Flax/PLA also starts decompose at lower temperature (199^{o}C) than the control (252^{o}C) similar to other FR-Flax/PLA samples, showing the first mass loss step between 199 – 290^{o}C with the DTG max at 273^{o}C and 21.5% mass

loss. The second mass loss step occurs in the range of 290 – 392^{o}C, which is accompanied by the exothermic DTA peak at 379^{o}C, representing the main decomposition of GDP-Flax/PP. In the third mass loss step, the decomposition occurs from 392^{o}C to 614^{o}C, producing 7.6% charred residue. This show that GDP improved the thermal stability of flax/PLA to decompose with more char formation as seen from the significant increase in charred residue in GDP-Flax/PLA (7.6%) in comparison to the control (0.8%). This as explained earlier is due to the condensed phase activity of GDP, as on heating the GDP releases phosphoric acid, which reacts with flax/PLA composite, and hence leads to change in decomposition pathway of flax/PLA to yield more char. Similar to other FR treated flax/PLA, the relatively low thermal stability of GUP causes the GDP-Flax/PLA to start losing mass at lower temperature (192^{o}C) than the control (252^{o}C), and then decomposes with three mass loss steps. On comparing this to the control, the results show that GUP improved the char formation of flax/PLA significantly similar to that observed in other condensed phase FRs in this study, i.e. AS and GDP flame retardants.

5.2.2.4. Effect of FR on different components of the composites

To have better understanding that whether the FR reacts only with flax or with PP and PLA as well, flax fabric, PP and PLA fibres (in sliver form) were treated with GUP to have a similar FR pickup as in above section. Results are given in Table 5.17. The TGA curves of effect of GUP on flax, PP and PLA are shown in Figure 5.13.

Table 5.17: FR pickup of flax, PP and PLA treated with GUP flame retardant

Sample	FR pickup (%)	P content (%)
GUP-Flax	10.4	0.89
GUP-PP	9.9	0.85
GUP-PLA	10.1	0.86

As can be seen from Figure 5.13 (a), the GUP interacts with flax at temperature above 220^{o}C, helping in improving char formation from 330^{o}C upward. In GUP treated PP (GUP-PP), GUP though decomposes between 183 - 220^{o}C, does not seem to interact with PP up to 310^{o}C, above which increases char formation. With PLA however, there seems to be interaction between 285 - 388^{o}C, i.e. at the same temperature as decomposition of PLA, residual char above 400^{o}C is however not affected.

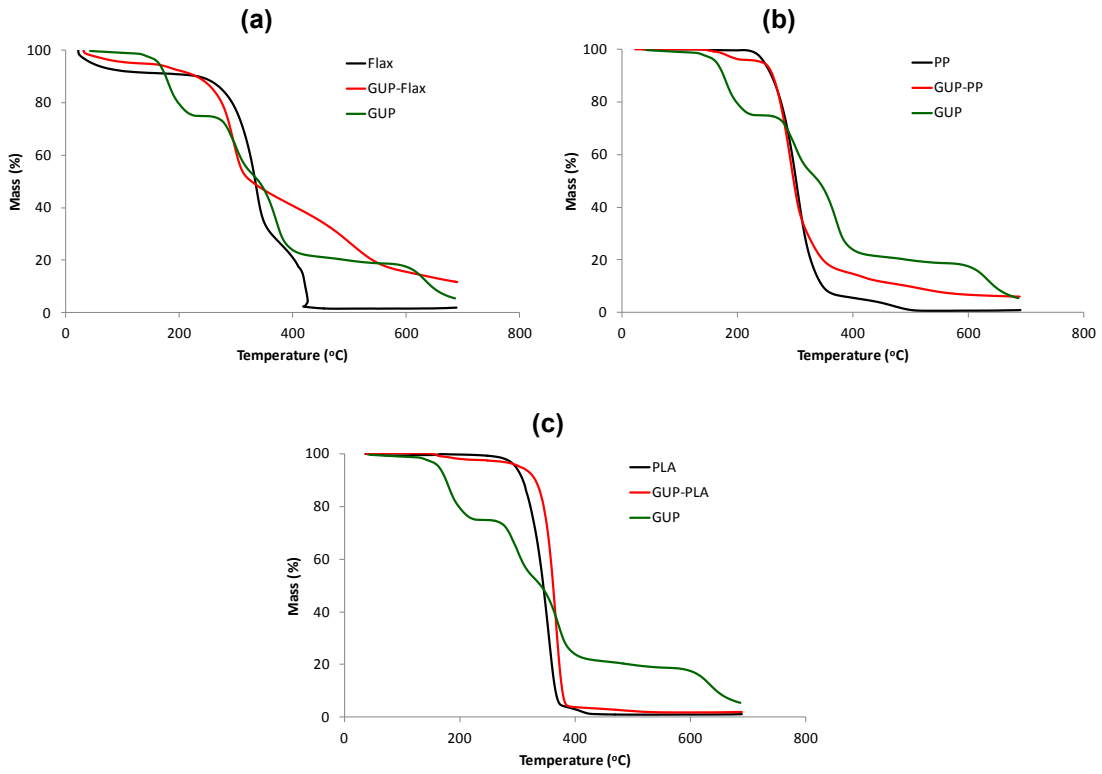

Figure 5.13: TGA curves of control and GUP treated (a) flax, (b) PP and (c) PLA in air

5.2.3 Conclusions

The use of FRs significantly improved the fire retardancy of flax/PP composites. The efficiency of FRs however varies depending upon the type of FR used. Guanylurea methylphosphonate (GUP) was seen to be the most effective FR to flame retard flax/PP composites, as it was the only FR in this study that could improve the UL-94 rating of flax/PP from 'fail' in the control to V-0 rating in GUP-Flax/PP. For flax/PLA laminates also, all FRs significantly reduced the flammability of flax/PLA, and their efficiencies were more pronounced than in flax/PP composites. However, GUP showed the best performance in comparison to other FRs. Although GUP provided great fire retardant properties to the composite laminate, it also caused reduction in the mechanical properties of the resulting laminates. The GUP reduced mechanical performance of flax/PP laminates due to a loss of mechanical properties of flax fibres after treatment with acidic GUP solutions (pH 3.3), and also the FR interfered with the fibre/matrix interfacial adhesion, whereas flax/PLA laminate, which is considered to be more reactive, was more severely affected by the presence of GUP due to the combination of damage on flax fibres due to acidic FR solutions and a partial degradation of PLA caused by the liberated alkali products from the partial decomposition of GUP during laminate preparation. Hence, the optimisation of the GUP flame retardant formulation was therefore required to minimise the effect on mechanical properties of the laminates while the fire retardant efficiency is maintained.

Part 3

5.3 The effect of FR content on fire and mechanical performance of FR flax/PP and flax/PLA composites

As discussed above, GUP although provides significant improvement in fire retardancy to flax/PP and flax/PLA composites (i.e. V-0 rating in UL-94 test), it causes reduction in the mechanical properties of the derived composites. Hence, the focus in this section was to study the effect of different GUP contents on the fire and mechanical performance of FR treated flax/PP and flax/PLA composites in order to identify the optimised FR content that can significantly improve fire performance of their laminates, i.e. achieving V-0 rating, with a minimal effect on mechanical properties. Eight layered laminates of flame retardant flax/PP and flax/PLA composite containing different FR contents were prepared from the flax/PP and flax/PLA woven fabrics treated with different concentrations of GUP flame retardant solutions as shown in Table 5.18. The fire and mechanical performance of these prepared FR flax/PP and flax/PLA laminates were then investigated to study the effect of FR content.

Table 5.18: The FR contents on flame retarded flax/PP and flax/PLA fabrics

Sample	Applied GUP solutions		FR Cont.	P Cont.	N Cont.
	Conc. (wt-%)	pH	(%)	(%)	(%)
Flax/PP	-	-	-	-	-
GUP-Flax/PP_0.6P	10.0	3.36	7.0 ±0.7	0.6 ±0.1	1.0 ±0.1
GUP-Flax/PP_0.8P	15.0	3.34	9.6 ±0.8	0.8 ±0.1	1.4 ±0.1
GUP-Flax/PP_0.9P	17.5	3.33	10.8 ±0.5	0.9 ±0.1	1.5 ±0.1
GUP-Flax/PP_1.0P	20.0	3.30	11.2 ±2.1	1.0 ±0.2	1.6 ±0.3
Flax/PLA	-	-	-	-	-
GUP-Flax/PLA_0.4P	10.0	3.36	5.4 ±0.8	0.4 ±0.1	0.7 ±0.1
GUP-Flax/PLA_0.5P	12.5	3.35	6.4 ±0.7	0.5 ±0.1	0.8 ±0.1
GUP-Flax/PLA_0.6P	15.0	3.34	7.2 ±0.3	0.6 ±0.1	1.0 ±0.1
GUP-Flax/PLA_0.8P	20.0	3.30	9.9 ±1.4	0.8 ±0.1	1.4 ±0.2

5.3.1 Fire performance of FR flax/PP and flax/PLA composites

5.3.1.1 UL-94 test

The UL-94 results of control and FR treated flax/PP and flax/PLA laminates are reported in terms of UL-94 rating and rates of burning (vertical and horizontal orientations) in Table 5.19. The control flax/PP laminate failed the UL-94 rating test as discussed before, the specimen completely burnt up to the sample holder with the burning rate of 152.7 mm/min. On addition of GUP flame retardant, the flammability of flax/PP laminates was significantly reduced. As expected the efficiency of GUP was greater with the higher FR content in FR treated flax/PP laminates. As seen from Table 5.19, the addition of GUP on flax/PP laminates at 0.6 and 0.8% P contents significantly decreased the burning rates of flax/PP laminates by about 40 and 60%,

respectively, but still could not change the UL-94 rating of the laminates. When the GUP content on flax/PP laminates was further increased to at least 0.9% P, the laminates could then achieve V-0 rating.

Table 5.19: UL-94 results of control and FR treated flax/PP and flax/PLA laminates

Sample	Horizontal			Vertical			Rating
	B.Length (mm)	B.Time (s)	B.Rate (mm/min)	B.Length (mm)	B.Time (s)	B.Rate (mm/min)	
Flax/PP	100 ±1	284 ±13	21.4 ±0.9	100 ±1	41 ±5	152.7 ±12.1	Failed
GUP-Flax/PP _0.6P	100 ±1	456 ±12	13.0 ±0.8	100 ±1	64 ±7	88.3 ±8.1	Failed
GUP-Flax/PP _0.8P	100 ±1	617 ±19	9.3 ±0.5	100 ±1	101 ±11	56.3 ±3.1	Failed
GUP-Flax/PP _0.9P	11 ±3	271 ±33	2.4 ±0.3	-	-	-*	V-0
GUP-Flax/PP _1.0P	-	-	-**	-	-	-*	V-0
Flax/PLA	100 ±1	308 ±21	20.0 ±1.2	100 ±1	44 ±1	131.3 ±8.0	Failed
GUP-Flax/PLA_0.4P	-	-	-**	100 ±1	64 ±3	88.3 ±8.3	Failed
GUP-Flax/PLA_0.5P	-	-	-**	15 ±1	16 ±1	55.7 ±0.1	V-1
GUP-Flax/PLA_0.6P	-	-	-**	-	-	-**	V-0
GUP-Flax/PLA_0.8P	-	-	-**	-	-	-**	V-0

* The flame went out before reaching the timing mark after removal of the burner

** Sample did not ignite, and hence the burning rate could not be calculated

The control flax/PLA laminate as discussed before has lower flammability as compared to the control flax/PP, but it also failed the vertical rating test and burned completely with burning rate of 131.3 mm/min. The burning rate of flax/PLA laminate was significantly reduced with the addition of GUP at 0.4 and 0.5% P contents, in particular horizontal test where the rates of burning could not be calculated as the flame went out before reaching the timing mark. Moreover, to achieve V-0 rating, flax/PLA laminate required only 0.6% P of GUP content.

5.3.1.2 Cone calorimetry

The cone calorimetric results of flame retarded flax/PP and flax/PLA laminates with different FR contents tested at 35 kW/m^2 are graphically presented in Figure 5.14 and 5.15. The derived results from the curves are given in Table 5.20.

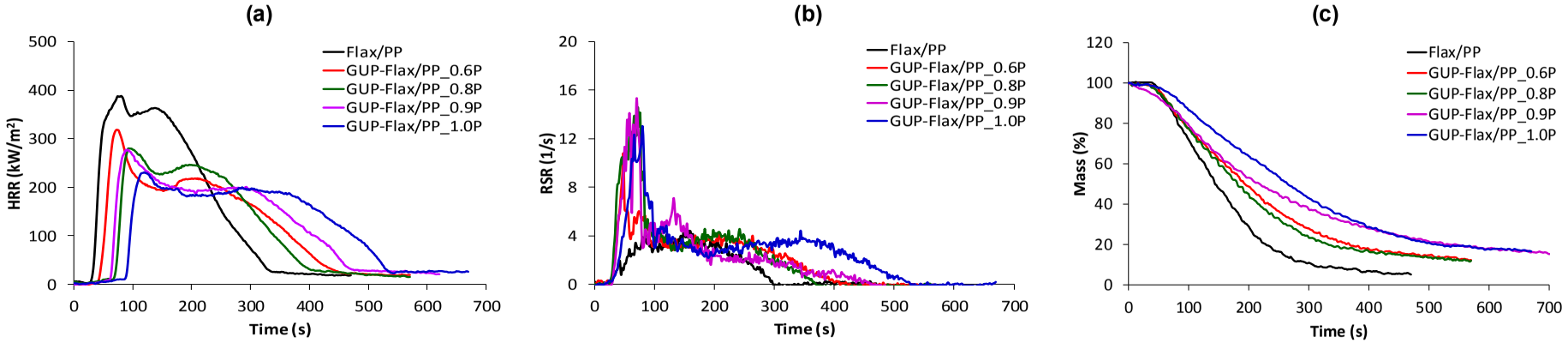

Figure 5.14: Cone calorimetric results of control and FR treated flax/PP at 35 kW/m^2: (a) HRR, (b) RSR and (c) mass loss curves as a function of time

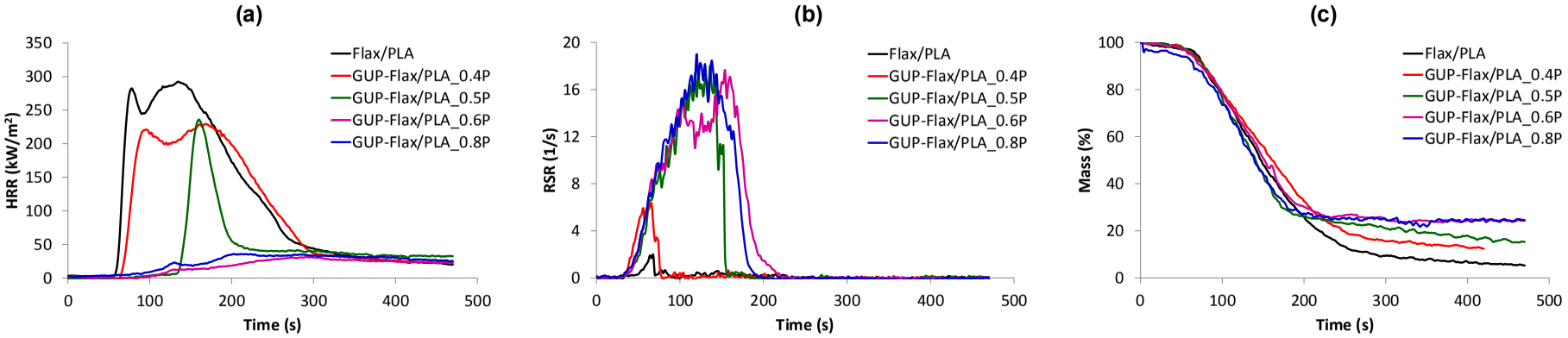

Figure 5.15: Cone calorimetric results of control and FR treated flax/PLA at 35 kW/m^2: (a) HRR, (b) RSR and (c) mass loss curves as a function of time

Table 5.20: Cone calorimetric results of FR containing flax/PP and flax/PLA laminates at 35 kW/m^2

Sample	TTI (s)	FOT (s)	Peak 1		Peak 2		THR (MJ/m^2)	EHC (MJ/kg)	TSR (L)	Yield (%)
			T_{PHRR} (s)	PHRR (kW/m^2)	T_{PHRR} (s)	PHRR (kW/m^2)				
Flax/PP	36 ±1	327 ±1	78 ±3	391 ±2	141 ±1	364 ±23	76 ±2	27 ±1	704 ±131	5.1 ±0.9
GUP-Flax/PP_0.6P	54 ±8	434 ±23	74 ±1	319 ±15	205 ±7	220 ±1	70 ±6	25 ±1	1146 ±41	12.3 ±1.0
GUP-Flax/PP_0.8P	79 ±4	397 ±11	97 ±7	286 ±3	196 ±6	247 ±5	65 ±1	22 ±1	1350 ±132	12.0 ±0.5
GUP-Flax/PP_0.9P	74 ±2	525 ±71	105 ±18	279 ±1	292 ±1	201 ±7	71 ±1	22 ±1	1509 ±334	15.7 ±3.9
GUP-Flax/PP_1.0P	90 ±8	535 ±8	113 ±10	247 ±24	297 ±16	211 ±16	80 ±5	21 ±1	1625 ±261	16.6 ±1.3
Flax/PLA	66 ±2	265 ±3	78 ±2	283 ±4	135 ±1	293 ±10	49 ±2	13 ±1	61 ±20	5.2 ±1.7
GUP-Flax/PLA_0.4P	71 ±5	290 ±2	94 ±3	236 ±9	165 ±7	232 ±2	41 ±1	12 ±1	194 ±26	12.4 ±0.1
GUP-Flax/PLA_0.5P	148 ±7	209 ±8	160 ±1	223 ±49	-	-	19 ±5	4 ±1	1210 ±364	16.0 ±2.1
GUP-Flax/PLA_0.6P	-	-	294 ±6	31 ±2	-	-	8 ±1	2 ±1	1629 ±43	24.4 ±6.6
GUP-Flax/PLA_0.8P	-	-	311 ±33	39 ±7	-	-	10 ±1	3 ±1	1591 ±96	25.1 ±6.5

The cone calorimetric results in Table 5.20 show that at 0.6% P content of GUP in flax/PP laminate, the TTI was delayed from 36 s of the control to 54 s, and the PHRR and THR were reduced by about 18% and 10% respectively compared to the control. With the increase in amount of GUP content, the TTI of flax/PP was further delayed, reaching 90 s in GUP-Flax/PP_1.0P. The change in each parameter as a function of phosphorus content is shown in Figure 5.16 (a). Similar trend is also seen in the reduction in PHRR and the increase in char residue, the higher GUP content on the laminates show better efficiency than the lower ones, Figure 5.16 (b) and (c).

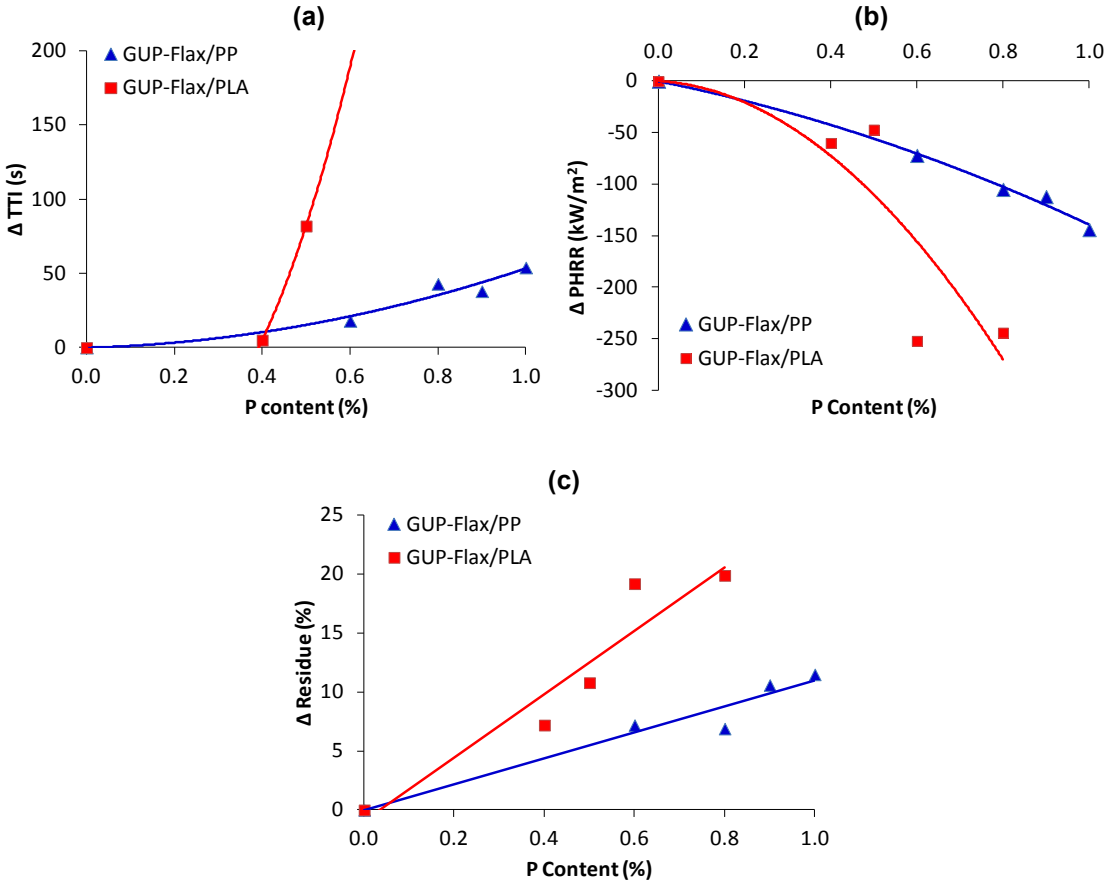

Figure 5.16: The change in TTI, 1st PHRR, and charred residue of GUP treated flax/PP and flax/PLA samples compared to the control at 35 kW/m² as a function of phosphorus content

The GUP flame retardant significantly enhanced the fire performance of flax/PLA laminates, and the effect was more pronounced than that using in flax/PP as discussed before and also seen from Figure 5.16. The results in Table 5.20 show that the addition of GUP at 0.4% P content shows marginal effect on the TTI of flax/PLA, and decreased PHRRs by about 20% in both peaks. On increasing the GUP content to 0.5% P level, the fire performance of flax/PLA was further enhanced as seen by significant delay in TTI (148 s), and also the change of burning behaviour from double peaks of HRR to a single peak, Figure 5.15 (a), which as explained earlier it is due to the significant improvement in the char formation of GUP-Flax/PLA_0.5P (16.0% compared to 5.2% in the control) could provide greater barrier properties and protect the

remaining materials from further combustion. With the further increase of GUP content to 0.6 and 0.8% P, FR efficiency of GUP is enough to prevent ignition, Figure 5.15 (a).

5.3.2 Mechanical performance of FR flax/PP and flax/PLA composites

The mechanical performance of control and FR treated flax/PP and flax/PLA laminates are reported in tensile, flexural and impact modes in Table 5.21. The tensile, flexural and impact modulus of these laminates were calculated from the elastic region of the stress-strain curves.

Table 5.21: Mechanical properties of control and FRs contained flax/PP and flax/PLA laminates

Sample	FR cont (wt-%)	Tensile properties		Flexural Modulus (GPa)	Impact Modulus (GPa)
		Modulus (GPa)	Strength (MPa)		
Flax/PP	-	6.0 ±0.3	44 ±12	6.3 ±0.5	14.9 ±0.4
GUP-Flax/PP_0.6P	7.0 ±0.7	6.4 ±0.5	53 ±4	7.9 ±0.2	13.9 ±0.4
GUP-Flax/PP_0.8P	9.6 ±0.8	5.8 ±0.4	44 ±3	6.7 ±1.0	14.1 ±0.2
GUP-Flax/PP_0.9P	10.8 ±0.5	5.7 ±0.5	40 ±5	6.5 ±0.2	13.8 ±0.1
GUP-Flax/PP_1.0P	11.2 ±2.1	3.4 ±0.1	35 ±1	3.3 ±0.5	10.2 ±0.8
Flax/PLA	-	8.5 ±0.3	92 ±3	11.3 ±0.5	15.4 ±1.8
GUP-Flax/PLA_0.4P	5.4 ±0.8	8.8 ±1.1	40 ±1	12.0 ±0.4	11.2 ±0.1
GUP-Flax/PLA_0.5P	6.4 ±0.7	8.8 ±0.1	42 ±2	12.0 ±1.1	10.9 ±0.4
GUP-Flax/PLA_0.6P	7.2 ±0.3	7.4 ±0.3	39 ±1	8.3 ±1.1	8.6 ±0.1
GUP-Flax/PLA_0.8P	9.9 ±1.4	5.0 ±0.4	29 ±1	5.2 ±0.5	4.6 ±0.6

Note: Fibre volume fractions in all flax/PP samples are ~40%, and all flax/PLA are ~60%.

In tensile mode, the properties of control flax/PP laminate are 6.0 GPa of modulus and 44 MPa of tensile strength. On addition of GUP flame retardant, the tensile modulus of flax/PP laminate gradually decreased with increasing content of GUP, Table 5.21. However, the degree in reduction of the tensile modulus was not linear to the increase of GUP content, Figure 5.17, as can be seen that the tensile modulus of flax/PP gradually reduced from 6.0 GPa of the control to 5.7 GPa of GUP-Flax/PP_0.9P with 10.8 wt-% of GUP content, and then significantly dropped to 3.4 GPa when the GUP content reached to 11.2 wt-% in GUP-Flax/PP_1.0P laminate. In terms of the effect of GUP on tensile strength of flax/PP, the GUP also decreased the tensile strength of flax/PP laminates, and the reduction was further with an increase amount of GUP on the laminates, Table 5.21. As the tensile properties of composites are reinforcing fibre dependent, the reduction in tensile properties of flax/PP could be explained by a change in flax properties after treatment with GUP solution [12]. Since a strong acid can cause damage to cellulose in flax fibre and leads to a loss of fibre properties, the pH of GUP solutions is an important parameter to explain the reduction of tensile properties of FR treated laminates [13]. As seen from Table 5.17, the pH values of GUP solutions decrease with an increase of GUP concentration, indicating the solution becomes more acidic. Therefore, at higher concentration

of GUP solution, the damage on flax fibre could be more severe, and hence results in a larger reduction of tensile properties of the FR treated flax/PP laminates.

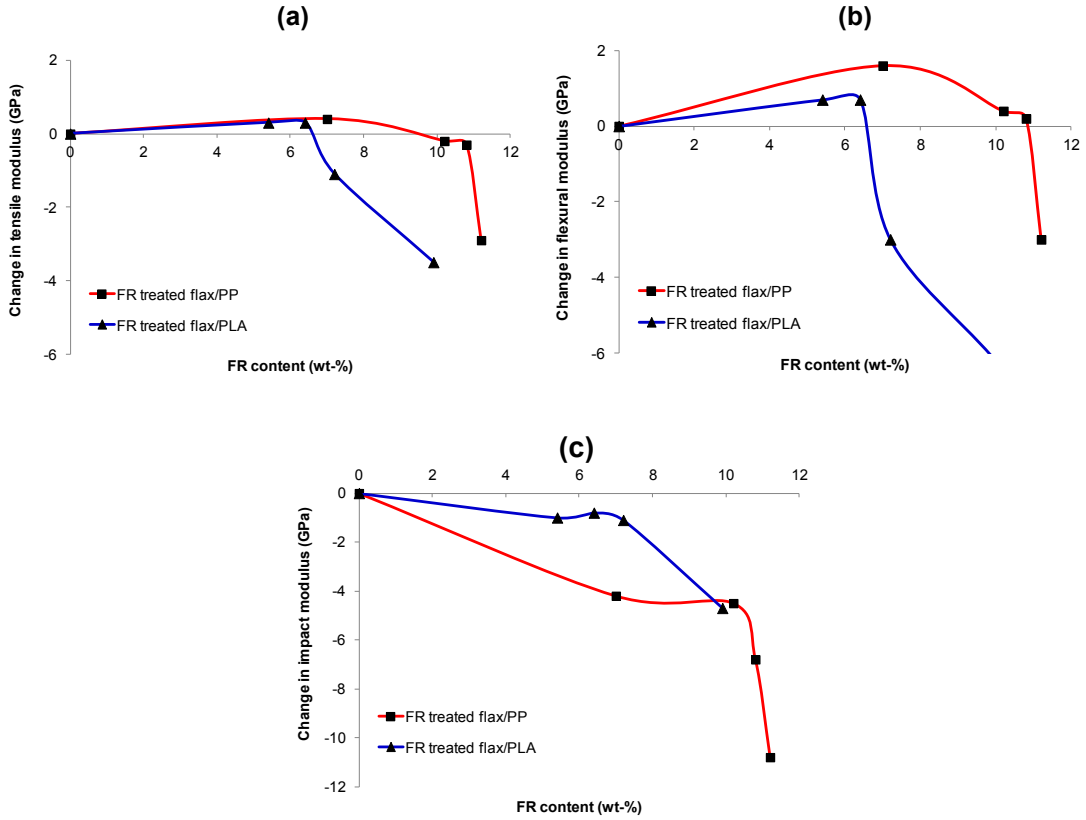

Figure 5.17: The change in (a) tensile, (b) flexural, and (c) impact modulii of FR treated flax/PP and flax/PLA laminates at different FR contents compared to the control samples (calculated by $E_{\text{of FR laminates}} - E_{\text{of control}}$*)*

The flexural and impact modulus of control flax/PP laminate are 6.3 and 15.4 GPa respectively. The addition of GUP at 7.0 wt-% content slightly increased the flexural modulus from 6.3 GPa of the control flax/PP to 7.9 GPa of GUP-Flax/PP_0.6P. However, once the GUP content was further increased, the flexural modulus of flax/PP started to decrease gradually to 6.7 and 6.5 GPa with the presence of GUP at 9.6 and 10.8 wt-% respectively, and then when the GUP content reached to 11.2 wt-% the flexural modulus was further decreased significantly to 3.3 GPa. This can be explained by the fact that although flexural properties of composites are generally polymer matrix dependent, the fibre-matrix interfacial adhesion could also affect the properties as the low adhesion can lead to a delamination failure, and hence cause a reduction in the flexural properties [12,41]. Since PP having high chemical resistant properties, the reduction in flexural properties of FR treated flax/PP could be due to a decrease in the fibre/matrix interfacial adhesion of the laminates. Impact results of GUP treated flax/PP composites also show similar trend as observed in flexural properties as the impact modulus of flax/PP is gradually decreased with the increased GUP content on the composites until reaching 10.8 wt-% content, then the reduction in the impact modulus become very severe, Figure 5.17.

The addition of GUP on flax/PLA laminates at low content, 5.4 and 6.4 wt-%, slightly increased the tensile modulus from 8.5 GPa of the control sample to 8.8 GPa, and then the modulus was gradually decreased to 7.4 and 5.0 GPa when the GUP content was increased to 7.2 and 9.9 wt-% respectively. The GUP significantly decreased the tensile strength, which is more than 50% reduction in all samples. The results in Table 5.21 also show that the tensile properties of flax/PLA laminates were more severely affected by the presence of GUP compared to flax/PP as it can seen that at the same GUP content on the laminates, the reduction of tensile properties, in particular tensile strength, of FR treated flax/PLA laminates was larger than those FR treated flax/PP laminates as explained before is due to reaction of GUP with PLA. From Table 5.21, the results showed that GUP also causes a reduction in flexural properties of FR treated flax/PLA, and the reduction was more severely developed at higher GUP content, especially at the GUP content above 7.2 wt-% the flexural modulus of flax/PLA was significantly reduced by more than 50%, Figure 5.17 (b). The effect of GUP on impact properties was similar to that on flexural as the impact modulus of the laminates was gradually reduced with the increased amount of GUP content on the laminates, Table 5.21. Moreover, at the same GUP content on the laminates, GUP causes a larger reduction in impact properties of flax/PLA laminates in comparison to that of flax/PP.

5.3.3 Conclusions

Guanylurea methylphosphonate (GUP) could significantly improve the fire performance of flax/PP and flax/PLA laminates, V-0 UL-94 rating could be achieved with 0.9%P in flax/PP and 0.6%P in flax/PLA, respectively. The FR efficiency of GUP was better when used in laminates with PLA polymer matrix which required a lower amount of GUP than those with PP matrix to achieve the same level of fire performance. It was also seen that the efficiency of GUP as a fire retardance was not in a linear relation to increasing GUP content. The cone calorimetric results showed that the fire performance of laminates improved with an increasing amount of GUP content on the laminates until reaching a certain level, i.e. 0.9% P of GUP content for flax/PP and 0.6% P for flax/PLA, and then further increase of GUP did not provide any further significant improvement. On the other hand, the increase of GUP content caused a significant reduction in mechanical properties of the laminates, especially at high GUP contents. Based on these results, the optimised GUP contents for producing flame retardant flax/PP and flax/PLA composite laminates could be identified as 0.9% P and 0.6% P respectively, as above these levels, the GUP causes an extra loss of mechanical properties without any further significant improvement in fire performance of the composites.

Part 4

5.4 The effect of pH of FR solution on fire and mechanical performance of FR flax/PP and flax/PLA composites

As the results in the previous section show that one of the reasons that causes reduction in mechanical properties of the GUP treated flax/PP and flax/PLA composites was the damage on flax fibre caused by the acidity of the applied FR solution (i.e. GUP solution with pH 3.2), the focus in this section was to study the effect of pH of GUP solution used for treating flax/PP and flax/PLA fabrics on the fire and mechanical performance of the derived composites in order to further optimise the FR formulation for preparing FR-flax/PP and flax/PLA composites. To adjust the pH of the solution, sodium acetate (NaOAc) was added into the solution to work as a buffering agent to reduce the acidity of the GUP solution. The preliminary study was conducted by testing for the tensile strength of flax fabric treated with 20 wt-% GUP solution at different pH values (Figure 5.18), in order to identify the suitable pH value of the solution that causes minimum effect on mechanical properties of flax fibre.

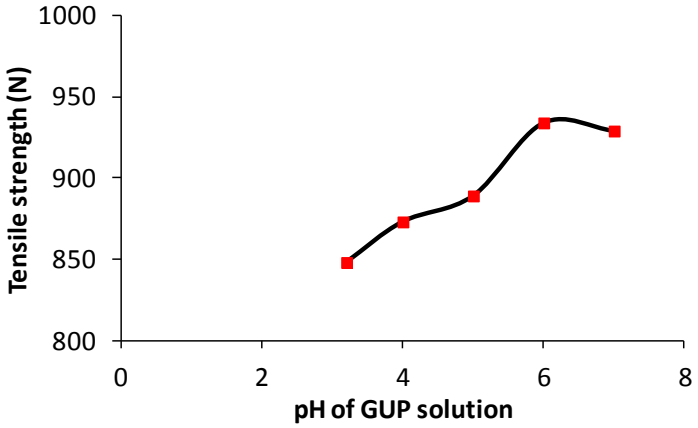

Figure 5.18: Tensile strength (N) of flax fabrics treated with GUP solution at different pH values

The results in Figure 5.18 show that the tensile strength of GUP treated flax fabric gradually increases with the increase in pH value of the GUP solution (i.e. less acidic), and then the increase becomes marginal when the pH value increases above 6.0. Hence, to study the effect of pH of the GUP solution on the fire and mechanical performance of GUP treated flax/PP and flax/PLA composites, the composites were prepared from the fabrics treated with GUP solutions of pH 3.2 (i.e. without pH modification as in earlier section) and pH 6.0. Based on the results in *Section 5.3*, the GUP contents on the treated flax/PP and flax/PLA fabrics were adjusted at 0.9 and 0.6% P levels, respectively, as these are minimum levels of the GUP content that the composites require in order to pass V-0 rating in UL-94 test. The details of the GUP solutions and the actual GUP content on the fabrics are given in Table 5.22.

Table 5.22: Sample details of flax/PP and flax/PLA fabrics treated with GUP solution at different pH values

Sample	FR solution			FR treated fabrics		
	GUP Conc. (wt-%)	NaOAc (g/100g sol.)	pH of solution	Solid Cont. (%)	GUP Cont (%)	P Cont (%)
GUP-Flax/PP (pH3.2)	18	-	3.2	11.3 ±1.0	11.3 ±1.0	0.95 ±0.06
GUP-Flax/PP (pH6.0)	20	18	6.0	20.6 ±0.7	10.8 ±0.4	0.93 ±0.03
GUP-Flax/PLA (pH3.2)	13	-	3.2	8.3 ±0.5	8.3 ±0.5	0.71 ±0.04
GUP-Flax/PLA (pH6.0)	15	18	6.0	17.5 ±0.6	8.0 ±0.3	0.68 ±0.02

The composites from these treated fabrics were prepared by melt-pressing eight layers of the fabrics into 3 mm thick laminates, and tested for fire and mechanical properties.

5.4.1 Fire performance of FR flax/PP and flax/PLA composites

The flammability of GUP treated flax/PP and flax/PLA composites prepared from the fabrics listed in Table 5.22 were evaluated by using UL-94 and cone calorimetry.

Table 5.23: UL-94 results of control and GUP treated flax/PP composites

Sample	Horizontal			Vertical			Rating
	B.Length (mm)	B.Time (s)	B.Rate (mm/min)	B.Length (mm)	B.Time (s)	B.Rate (mm/min)	
Flax/PP	100 ±1	258 ±1	24 ±2	100 ±1	43 ±4	146 ±34	Failed
GUP-Flax/PP (pH3.2)	-	-	-	-	-	-	V-0*
GUP-Flax/PP (pH6.0)	100 ±1	503 ±1	12 ±1	100 ±1	61 ±13	105 ±31	Failed

* Sample did not ignite

The UL-94 results in Table 5.23 show that the use of GUP solution without buffering agent (sodium acetate, NaOAc) to prepare FR treated flax/PP composite could achieve V-0 rating, as reported previously. With the addition of NaOAc to adjust the pH of the GUP solution (pH 6.0), the efficiency of GUP flame retardant was reduced as can be seen that the vertical rating is reduced from V-0 rating in GUP-Flax/PP (pH 3.2) to 'fail' in GUP-Flax/PP (pH 6.0), the sample burned up to the sample holder with the rate of burning of 105 mm/min. The cone colorimetric results at 35 kW/m^2 in Table 5.24 show similar trend as observed in the UL-94 test. With the addition of NaOAc, GUP-Flax/PP (pH 6.0) ignited at 46 s, and burned with PHRRs of 300 and 292 kW/m^2 producing 112 MJ/m^2 THR. These results show that NaOAc decreased the FR performance of GUP as shown by the reduction in the TTI from 60 s in the GUP-Flax/PP (pH 3.2) to 46 s in GUP-Flax/PP (pH 6.0), and the increase in the second PHRR from 262 to 292 kW/m^2. Moreover, the presence of NaOAc also prolongs the burning time of composites (Figure 5.19 (a)), hence resulting the higher THR in the GUP-Flax/PP (pH 6.0) as compared to GUP-Flax/PP (pH 3.2). This could be due to the reason that on heating the phosphoric acid produced from GUP not only reacts with composite's components through phosphorylation, but also could

also undergoes ion-exchange with sodium ion of NaOAc which lead to a formation of metal phosphate [42,43], hence leading to the reduction in the FR performance of GUP in GUP-Flax/PP (pH 6.0) in comparison to the GUP-Flax/PP (pH 3.2).

Table 5.24: Cone calorimetric results of control and GUP treated flax/PP composites at 35 kW/m^2

Sample	TTI	Peak 1		Peak 2		THR	EHC	TSR	Yield
	(s)	T_{PHRR} (s)	PHRR (kW/m^2)	T_{PHRR} (s)	PHRR (kW/m^2)	(MJ/m^2)	(MJ/kg)	(litre)	(%)
Flax/PP	35 ±1	78 ±6	498 ±21	117 ±1	455 ±6	90 ±1	30 ±1	755 ±82	2.1 ±0.1
GUP-Flax/PP (pH3.2)	60 ±4	79 ±4	297 ±11	151 ±16	262 ±4	91 ±3	26 ±1	1470 ±41	14.8 ±1.2
GUP-Flax/PP (pH6.0)	46 ±4	82 ±3	300 ±1	184 ±6	292 ±7	112 ±5	29 ±1	1370 ±80	15.1 ±0.8

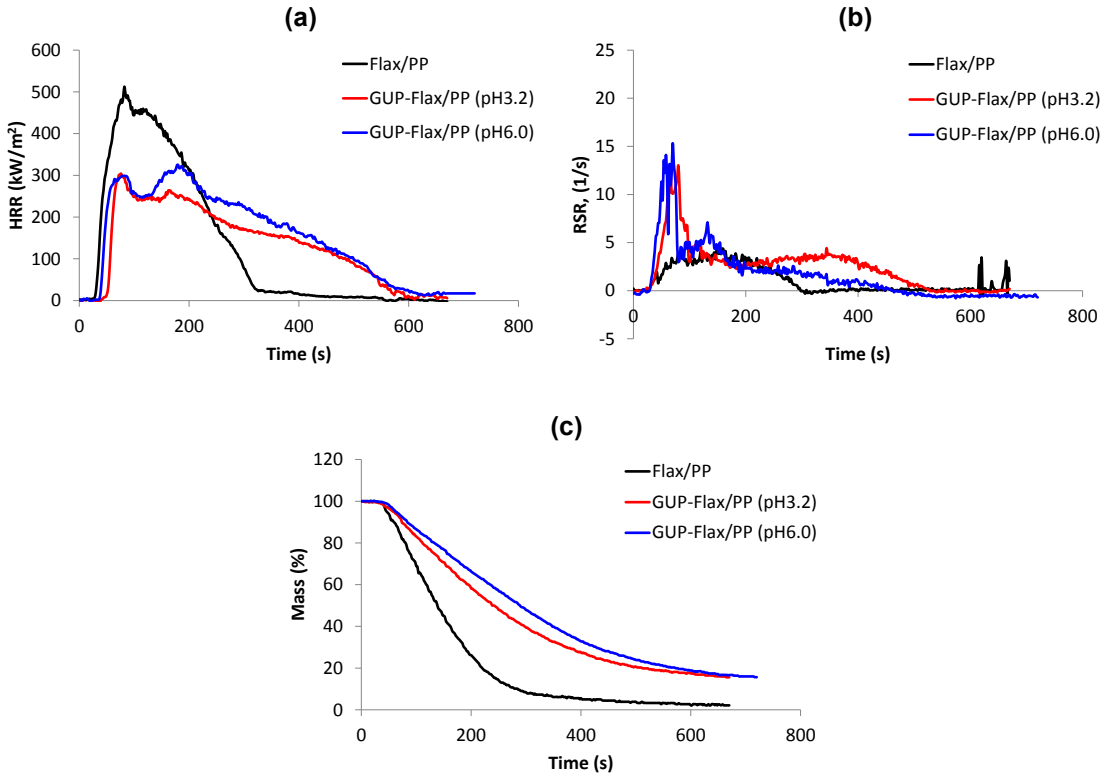

Figure 5.19: (a) HRR, (b) RSR and (c) mass loss curves of control and GUP treated flax/PP composites at 35 kW/m^2

In case of flax/PLA composites, with the use of NaOAc in the GUP solution, the results show similar trend as observed in flax/PP samples that the presence of NaOAc increased the flammability of GUP-Flax/PLA from V-0 in GUP-Flax/PLA (pH 3.2) to 'fail' in GUP-Flax/PLA (pH 6.0).

Table 5.25: UL-94 results of control and GUP treated flax/PLA composites

Sample	Horizontal			Vertical			Rating
	B.Length (mm)	B.Time (s)	B.Rate (mm/min)	B.Length (mm)	B.Time (s)	B.Rate (mm/min)	
Flax/PLA	100	274 ±5	22 ±2	100	43 ±4	151 ±45	Failed
GUP-Flax/PLA (pH3.2)*	-	-	-	-	-	-	V-0
GUP-Flax/PLA (pH6.0)	-**	-	-	100	91 ±4	66 ±3	Failed

Note: * Sample did not ignite
** The flame extinguished before reaching the timing mark

The cone calorimetric results show that at pH 3.2, the GUP helped in prevention of ignition in flax/PLA at 35 kW/m^2 heat flux. With the addition of NaOAc into the GUP solution, GUP-Flax/PLA (pH 6.0) ignited at 162 s, and burned with 72 kW/m^2 PHRR. Also, GUP-Flax/PLA (pH 6.0) shows slightly higher THR (9 MJ/m^2) in comparison to those of GUP-Flax/PLA (pH 3.2). This reduction in the fire retardancy of GUP-Flax/PLA (pH 6.0) as compared to GUP-Flax/PLA (pH 3.2) could be explained similar to that discussed in GUP-Flax/PP as the presence of NaOAc cause the decrease in the reaction between phosphoric acid, produced from GUP, and composite's component as phosphoric acid also react with sodium ion from NaOAc through ion-exchange reaction to form metal phosphate.

Table 5.26: Cone calorimetric results of control and GUP treated flax/PLA composites at 35 kW/m^2

Sample	TTI	Peak 1		Peak 2		THR	EHC	TSR	Yield
	(s)	T_{PHRR} (s)	PHRR (kW/m^2)	T_{PHRR} (s)	PHRR (kW/m^2)	(MJ/m^2)	(MJ/kg)	(L)	(%)
Flax/PLA	42 ±1	61 ±1	302 ±2	93 ±1	345 ±15	57 ±6	16 ±1	40 ±1	2.9 ±0.4
GUP-Flax/PLA (pH3.2)*	-	-	-	-	-	7 ±1	2 ±1	1540 ±121	16.8 ±0.2
GUP-Flax/PLA (pH6.0)	162 ±1	170 ±3	72 ±3	-	-	9 ±1	3 ±1	1380 ±70	17.1 ±1.5

* Sample did not ignite

5.4.2 Mechanical performance of FR flax/PP and flax/PLA composites

The mechanical properties of control and GUP treated flax/PP and flax/PLA composites were evaluated in tensile and flexural modes, the results in term of modulus and strength of these composites are reported in Table 5.27.

Table 5.27: Mechanical properties of control and GUP treated flax/PP and flax/PLA composites

Sample	Tensile properties		Flexural properties	
	Modulus (GPa)	Strength (MPa)	Modulus (GPa)	Strength (MPa)
Flax/PP	7.1 ±0.4	79 ±6	7.8 ±0.5	71 ±1
GUP-Flax/PP (pH3.2)	5.5 ±0.7	56 ±6	7.8 ±0.5	67 ±1
GUP-Flax/PP (pH6.0)	5.8 ±0.1	49 ±3	7.8 ±0.1	77 ±2
Flax/PLA	10.2 ±0.1	141 ±2	14.1 ±0.7	159 ±1
GUP-Flax/PLA (pH3.2)	9.7 ±0.1	98 ±5	13.0 ±0.2	132 ±2
GUP-Flax/PLA (pH6.0)	9.9 ±0.2	66 ±4	5.4 ±0.3	54 ±2

Note: Fibre volume fractions in all flax/PP samples are ~40%, and all flax/PLA are ~60%.

The tensile properties in Table 5.27 show similar trend as observed in previous section that the addition of GUP at pH 3.2 causes reduction in tensile properties of flax/PP composites, i.e. tensile modulus reduced to 5.5 GPa (23% reduction) and strength to 56 MPa (30% reduction) as compared to the control. With the presence of NaOAc, the tensile properties of GUP-Flax/PP composites were slightly improved as shown by the increase in tensile modulus from 5.5 GPa in GUP-Flax/PP (pH 3.2) to 5.8 GPa in GUP-Flax/PP (pH 6.0), while no effect is seen in the tensile strength of the composites. Since the tensile properties of composites are fibre dependent properties, the improvement in the tensile properties of GUP-Flax/PP (pH 6.0) is due to the reduction in the acidity of the GUP solution used for treating flax/PP fabrics. As flax fibre can be hydrolysed and lose its mechanical strength under acidic condition, the reduction in acidity of the GUP+NaOAc solution could help to minimise the damage on flax fibre, and so the tensile properties of the derived composites. This therefore results in the improved tensile properties in GUP-Flax/PP (pH 6.0) in comparison to the GUP-Flax/PP (pH 3.2). In flexural mode, the addition of GUP with and without NaOAc did not affect the properties of flax/PP composites as can be seen that all control and GUP-Flax/PP samples show similar flexural properties of 7.8 GPa modulus and ~70 MPa strength. This is due to flexural properties of composites are matrix dependent, hence the effect from the changes in properties of flax fibre, which is a reinforcement, is minimum, and could not be seen in these samples.

In case of flax/PLA composites, the addition of GUP at pH 3.2 (without NaOAc) also causes reduction in tensile properties, i.e. tensile modulus reduced from 10.2 GPa in the control to 9.7 GPa in GUP-Flax/PLA (pH 3.2), and tensile strength from 141 MPa to 98 MPa. Similar to that discussed in flax/PP samples, this is due to the hydrolysis of flax fibre in the acidic condition of the GUP solution that causes a drop in mechanical properties of flax and its derived composites. With the use of NaOAc to adjust the pH of GUP solution, the results show that the tensile modulus of GUP-Flax/PLA was slightly improved from 9.7 GPa in GUP-Flax/PLA (pH 3.2) to 9.9 GPa in GUP-Flax/PLA (pH 6.0). The tensile strength however show contradictory results as the addition of NaOAc decreases the tensile strength of GUP-Flax/PLA (pH 3.2) from 98 MPa to 66 MPa in GUP-Flax/PLA (pH 6.0). The reduction in the tensile strength of GUP-Flax/PLA (pH6.0) is due to the reason that although the NaOAc help to reduce the damage on GUP treated flax fibres, as being alkali agent NaOAc also causes hydrolysis of ester group (-COO-) in chemical structure of PLA, hence resulting in the reduction in the mechanical strength of PLA and its composites. The flexural properties of control and GUP treated flax/PLA composites show that the presence of only GUP did not show significant effect on the flexural properties of flax/PLA as can be seen from slight reductions in flexural modulus (13.0 GPa) and strength (132 MPa) in GUP-Flax/PLA (pH 3.2) as compared to the control, Table 5.27. Whereas, with the addition of NaOAc to adjust the pH of the GUP solution, the reduction in GUP-Flax/PLA sample becomes significant as GUP-Flax/PLA (pH 6.0) shows much lower flexural modulus (5.4 GPa) and strength (54 MPa) than that observed in GUP-Flax/PLA (pH 3.2). This is due to hydrolysis of PLA caused by NaOAc, as being alkali, leading to the reduction in mechanical properties of PLA, and as flexural properties are matrix dependent, hence this

leads to the significant reduction in the flexural properties of GUP-Flax/PLA (pH 6.0) in comparison to GUP-Flax/PLA (pH 3.2).

5.4.3 Conclusions

The flammability and mechanical properties of GUP-flax/PP composites prepared from the flax/PP fabrics treated with GUP solution at different pH values (i.e. 3.2 and 6.0), results show that the use of sodium acetate (NaOAc) to reduce the acidity of GUP solution (pH 6.0) help in maintaining the mechanical properties of GUP treated flax/PP composites, particularly the tensile properties. The effect is however marginal. However, the addition of NaOAc to adjust the pH of GUP solution shows negative effect on the flammability as NaOAc increased the flammability of GUP-Flax/PP composites, especially in UL-94 test, where previous V-0 in GUP-Flax/PP (pH 3.2) was reduced to 'fail' in GUP-Flax/PP (pH 6.0). In the case of GUP-Flax/PLA, the results show that the addition of NaOAc into the GUP solution although reduced the acidity of the solution, but it show contradictory results to those observed in GUP-Flax/PP samples as NaOAc decreased the mechanical properties, especially in flexural mode. This is due to the NaOAc, an alkali agent, which can cause hydrolysis of PLA, hence resulting in the reduction in mechanical properties of PLA and the derived composites. The NaOAc also increased flammability of GUP-Flax/PLA similar to that observed in flax/PP samples, particularly causing 'fail' in previously achieved V-0 rating. Hence, it can be concluded that there is no benefit in using the NaOAc to reduce the acidity of GUP solution for preparing FR treated flax/PP and flax/PLA composites.

5.5 Overall Conclusions

The studies on the flame retardant flax/PP and flax/PLA composites prepared from flame retarded flax/PP and flax/PLA commingled fabrics in this chapter show that there is no need of the fabric pre-treatment (scouring process) prior to flame retardant treatment of the fabrics as this did not provide clear benefit on both fire and mechanical performance of the derived composites. To identify the effective flame retardants (FRs) for the composites, the fabrics were treated with different FRs without pre-treating prior to laminate preparation. It was observed that guanylurea methylphosphonate (GUP) was the most effective flame retardant in both composite flax/PP and flax/PLA composites; at 10 wt-% GUP content on the laminates both GUP-Flax/PP and GUP-Flax/PLA could pass V-0 rating in UL-94 test. GUP however caused reduction in mechanical properties of the composites, in particular flax/PLA. Hence, the formulation of GUP flame retardant was further optimised to minimise the effect on mechanical properties, while the fire performance (i.e. V-0 rating) was still remained. The optimised condition for flax/PP was 0.9% P content of GUP on the laminate, while for flax/PLA was 0.6% P content. Further to observe the effect of pH of GUP solution, sodium acetate (NaOAc) was used to reduce the acidity of the GUP solution, which slightly improved mechanical properties of GUP-Flax/PP, but caused the reduction in GUP-Flax/PLA due to NaOAc causing hydrolysis of PLA matrix. Sodium acetate however increased the flammability of GUP-Flax/PP and GUP-Flax/PLA composites,

especially causing the 'fail' in UL-94 vertical test. From all of these results, it was concluded that there is no benefit of adjusting pH of the GUP solution.

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Chapter 6: Surface modification of flax/PP and flax/PLA fabrics to improve fibre/matrix interfacial adhesion

In this chapter, different surface modification treatments of flame retarded flax/PP and flax/PLA woven fabrics have been attempted to improve fibre/matrix interfacial adhesion in the derived composites. These include silane treatment (Si), plasma treatment (Pm), and the combination of both**.** Firstly, flax/PP and flax/PLA fabrics without any FR treatment were treated with silane or plasma by using different conditions in order to identify an optimised condition for each type of treatment. The identified optimum conditions of silane and plasma treatments were used for treating flame retarded flax/PP and flax/PLA fabrics in order to produce FR treated flax/PP and flax/PLA laminates by using melt pressing technique as discussed in Chapter 3 *(Section 3.2.5).* The surface characterisation of silane and plasma/FR treated flax/PP and flax/PLA fabrics has been conducted by using Fourier transform infrared and scanning electron microscopies. The effect of the surface modification treatments on the fibre/matrix interfacial adhesion of FR treated flax/PP and flax/PLA laminates was studied by using peeling test, flexural (three-points bending) test, and fractured surface observations. Based on these results the most effective surface modification treatment for each of flame retardant (FR) treated flax/PP and flax/PLA has been identified.

6.1 Selection and optimisation of silane treatment

Silane treatment is commonly used in natural fibre composites to improve compatibility between two phases, i.e. reinforcing fibres and the polymer matrix [1,2]. This is due to the generic chemical structure of silane with the bi-functional groups, which can form bridge between the two phases. Silane coupling agents' generic structure is $R_{(4-n)}$-Si-$(R'X)_n$ where R and R' are alkoxy groups, X is an organofunctional group, and n = 1 or 2. The alkoxy group (R) can react with hydroxyl groups of natural fibres, whereas organofunctional group (X) has affinity to react with the polymer matrix, and hence working as a coupling agent to improve the compatibility between the two phases [1-3]. The efficiency of silane treatment on natural fibre/polymer matrix depends on the selection of silane chemical with suitable organofunctional group for each type of polymer matrix. In this study, vinyltriethoxysilane (VTS) in combination with dicumyl peroxide (10:1 by weight) was chosen for flax/PP, while, 3-aminopropyl triethoxysilane (APTES) was chosen for flax/PLA. The chemical structures of these silanes are given in Figure 6.1.

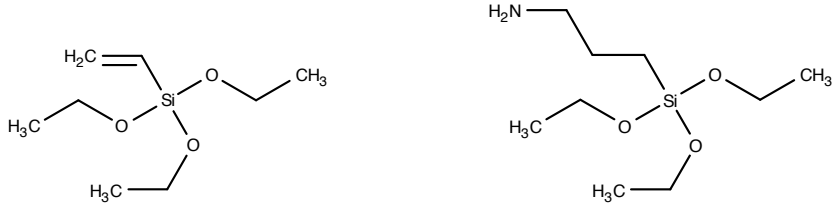

Figure 6.1: Chemical structures of (a): vinyltriethoxysilane and (b): 3-aminopropyl triethoxysilane

In order to identify the optimised concentration of silane on flax/PP and flax/PLA fabrics for each type of composites, flax/PP and flax/PLA woven fabrics were treated with 1, 2 and 3 wt-% silane solutions, and from these treated fabrics single layered laminates were prepared by melt-pressing. The silane contents on the treated flax/PP and flax/PLA fabrics, calculated from the weight changes of fabrics before and after silane treatment (explained in *Section 3.2.2.4*), are given in Table 6.1.

Table 6.1: Flax/PP and flax/PLA fabrics treated with different concentrations of silane solutions

Sample	Silane Treatment	Silane content on fabrics (%)
Flax/PP	1 wt-% VTS solution	0.6 ±0.1
	2 wt-% VTS solution	2.7 ±0.1
	3 wt-% VTS solution	4.5 ±0.1
Flax/PLA	1 wt-% APTES solution	1.2 ±0.1
	2 wt-% APTES solution	2.7 ±0.3
	3 wt-% APTES solution	4.2 ±0.1

Since tensile properties of composites are fibre reinforcement dependent, the fibre/matrix interfacial adhesion therefore plays an important role on the tensile properties. A greater interfacial adhesion provides better load-transfer between fibre and polymer matrix, and hence results in a higher tensile properties of composites [4]. The tensile properties of these silane treated single layered laminates were characterised in order to be used as indicative results to identify the optimised conditions. The tensile results of the single layered flax/PP and flax/PLA laminates are presented as stress-strain curves in Figure 6.2 and 6.3, respectively. The data interpreted from the curves, including tensile modulus (calculated from the elastic region of the tensile curves, as discussed in *Section 3.3.4.4*), and tensile strength, are reported in Table 6.2.

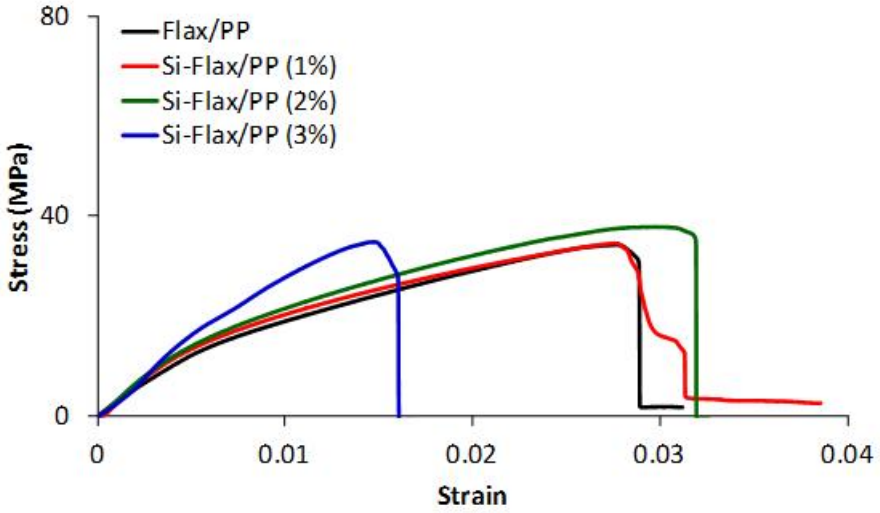

Figure 6.2: Tensile stress-strain curves of flax/PP single layered laminates from the fabrics treated with silane at different conditions

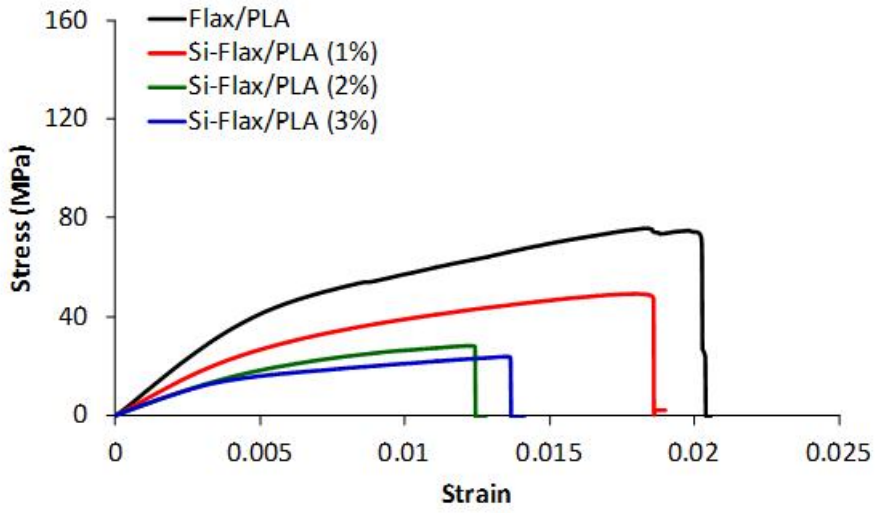

Figure 6.3: Tensile stress-strain curves of flax/PLA single layered laminates from the fabrics treated with silane at different conditions

Table 6.2: Tensile properties of single layered laminates from non-FR fabrics treated with silane

Sample	Treatment	Tensile Modulus (GPa)	Tensile Strength (MPa)	Strain-at-break (%)
Flax/PP	-	2.9 ±0.4	37 ±5	3.2 ±0.7
Si-Flax/PP (1%)	1 wt-% VTS Sol.	3.3 ±0.1	35 ±1	3.1 ±0.1
Si-Flax/PP (2%)	2 wt-% VTS Sol.	3.5 ±0.2	38 ±4	3.1 ±0.4
Si-Flax/PP (3%)	3 wt-% VTS Sol.	3.9 ±0.5	34 ±2	2.0 ±0.4
Flax/PLA	-	9.0 ±0.7	72 ±6	2.0 ±0.9
Si-Flax/PLA (1%)	1 wt-% APTES Sol.	5.6 ±0.9	42 ±7	1.4 ±0.4
Si-Flax/PLA (2%)	2 wt-% APTES Sol.	4.5 ±0.4	24 ±4	0.9 ±0.3
Si-Flax/PLA (3%)	3 wt-% APTES Sol.	3.5 ±0.5	19 ±5	1.0 ±0.4

6.1.1 Silane treated flax/PP single layered laminates

As seen from Table 6.2, the tensile modulus of control flax/PP single layered laminate is 2.9 GPa and tensile strength is 37 MPa. On applying 1 wt-% VTS solution (sample Si-Flax/PP (1%)), the modulus increased to 3.3 GPa, increasing further to 3.5 GPa and 3.9 GPa with 2 and 3 wt-% silane concentrations. The improvement in the fibre/matrix interfacial adhesion at a certain level also shows an effect on strain-at-break, as can be seen that the strain-at-break of flax/PP is little affected upto 2 wt-% silane concentration, but at 3 wt-% it is reduced. The tensile strength however remained unaffected. As mentioned above, the silane treatment works chemically to modify the surfaces of substrates, the improvement in tensile properties of flax/PP laminates with VTS treatment therefore could be explained by the changes in surface chemistry of flax/PP fabrics after silane treatment.

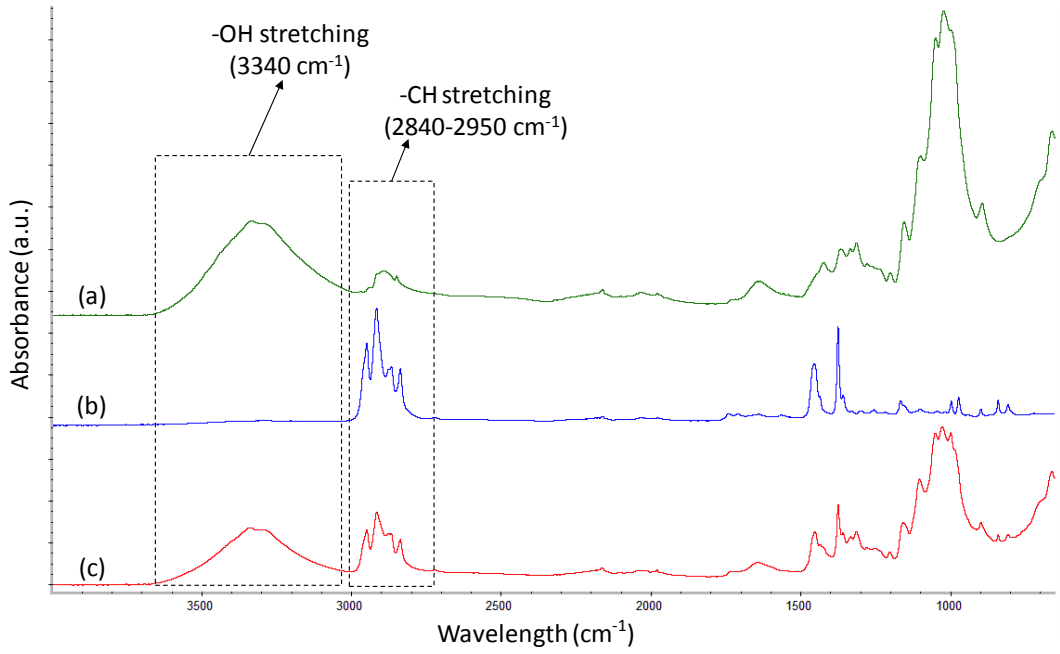

Figure 6.4: IR spectra of (a): flax fibres, (b): PP, and (c): commingled flax/PP woven fabric

In Figure 6.4, the IR spectra of flax, PP and flax/PP fabrics are presented. The IR spectrum of flax/PP fabrics shows the characteristic peaks of both flax and PP where the main peaks are at 3340 cm^{-1} (-OH stretching) corresponding to the reactive hydroxyl groups on the surface of flax fibres, and the superimposed IR absorption peaks between 2840-2950 cm^{-1} (-CH stretching) corresponding to $-CH_2-$ and $-CH_3$ of PP [5,6].

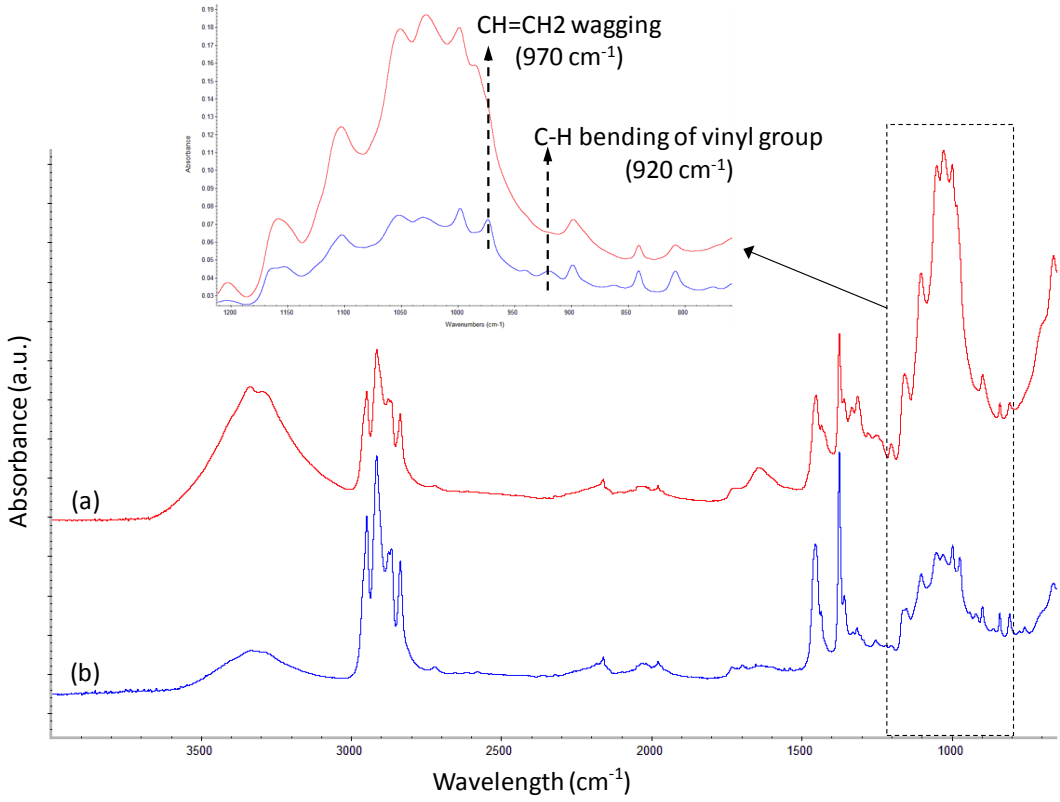

Figure 6.5: IR spectra of (a): untreated and (b): VTS treated flax/PP fabrics (3 wt-% VTS Sol.)

With the VTS treatment, the IR spectrum of flax/PP is slightly changed (Figure 6.5) shown by the reduction in the intensity of 3340 cm^{-1} (-OH stretching) peak, and the appearance of the peaks at 920 and 970 cm^{-1} (C-H bending and -CH=CH_2 wagging vibration, respectively) corresponding to the vinyl functional group of VTS [6]. This could be explained by the chemical reaction between VTS and flax/PP fabrics. In the presence of water (i.e. moisture absorbed in the fabric and the water in the VTS solution), the VTS undergoes hydrolysis, and forms the reactive silanol groups, Figure 6.6 (a). These silanol groups can be physically adsorbed on the surface of flax, and then chemically reacted with hydroxyl groups on the surface of flax fibres under heating to form covalent bonds between VTS and flax fibres as shown in Figure 6.6 (b) and (c) [1].

a) Hydrolysis of VTS silane

b) Adsorption of VTS on flax fibre via hydrogen bonding

c) Formation of covalent bonds between VTS and flax fibres

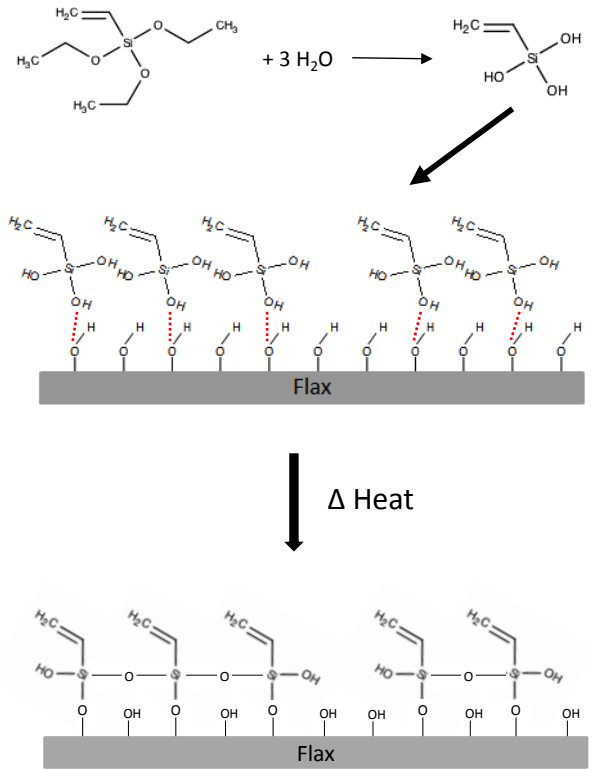

Figure 6.6: The schematic of the interaction between VTS silane and flax fibres in VTS treated flax/PP fabric

As a result of this reaction, the number of hydroxyl groups on the flax fibres decreases as shown by the reduction of the IR peak at 3340 cm^{-1} (-OH stretching). The vinyl groups of VTS are left on the surface of the flax fibre as can be seen the presence of vinyl groups (-CH=CH_2) characteristic peaks at 920 and 970 cm^{-1} in the spectrum of VTS treated flax/PP as compared to the untreated one, Figure 6.5. These vinyl groups can then interact with PP. The compatibility between flax and PP of VTS treated flax/PP is therefore improved, as compared to the untreated one. Moreover, with the addition of dicumyl peroxide (DCP) in the VTS solution, the vinyl groups on VTS treated flax could also chemically react with PP as the DCP could work as an initiator to create free radicals by abstracting hydrogen atoms from the polymer backbone of

PP as well as breaking the double bond of the vinyl groups on the surface of VTS treated flax [7-10]. These therefore lead to the chemical bonding between two radicals, and formation of a siloxane bridge between flax and PP as shown in Figure 6.7. As a result of the improvement of the compatibility and the formation of siloxane bridge between flax and PP matrix of VTS treated flax/PP, the fibre/matrix interfacial adhesion is therefore enhanced, and results in the increase in tensile properties of the VTS treated flax/PP laminates, as compared to the control sample Table 6.2 [11].

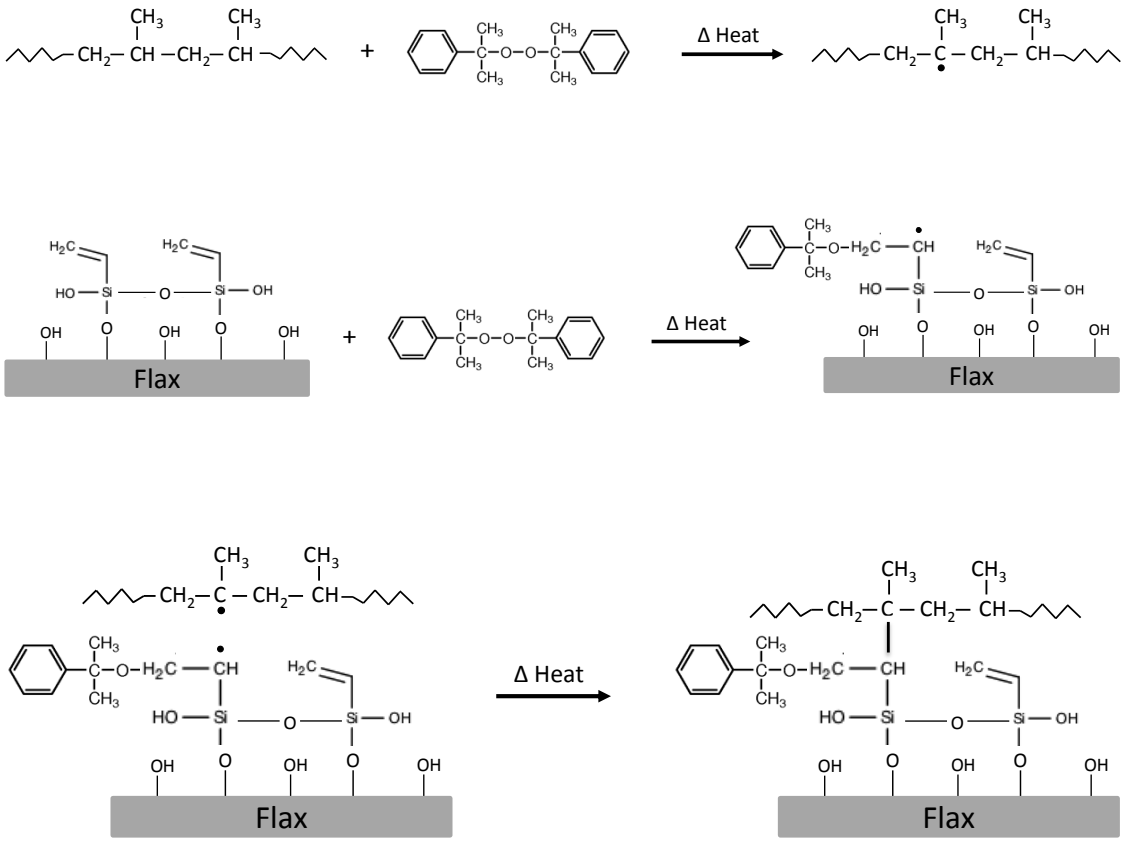

Figure 6.7: The formation of siloxane bridge between VTS treated flax and PP matrix

6.1.2 Silane treated flax/PLA single layered laminates

The silane treatment showed the opposite effect on flax/PLA laminates than in silane treated flax/PP. As can be seen from Table 6.2, the tensile modulus of flax/PLA composites decreased from 9.0 GPa to 5.6 GPa when treated with 1 wt-% concentration of APTES solution, and the reduction was more severe with a higher concentration of APTES solution, the tensile modulus decreased from 5.6 GPa of Si-Flax/PLA (1%) to 4.5 GPa and 3.5 GPa of Si-Flax/PLA (2%) and Si-Flax/PLA (3%) respectively.

Similar to the silane treated flax/PP, the effect of APTES on tensile properties of flax/PLA single layered laminates can be explained by the changes in surface chemistry of flax/PLA fabrics

after treatment. The IR spectra of flax fabric, PLA and flax/PLA commingled fabrics are shown in Figure 6.8. The IR spectrum of flax/PLA shows the combination of peaks of flax, at 3340 cm^{-1} (-OH stretching) corresponding to hydroxyl groups of flax, and that of PLA, i.e. 1749 cm^{-1} (C=O stretching) for the ester groups (-COO-), Figure 6.8.

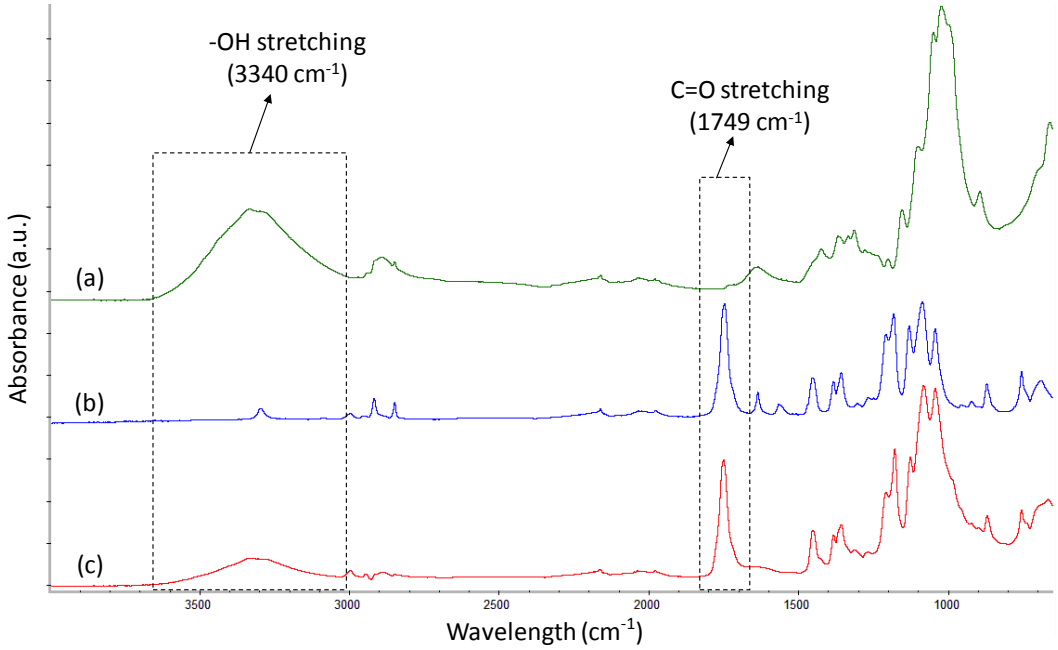

Figure 6.8: IR spectra of (a): flax fibres, (b): PLA, and (c): commingled flax/PLA woven fabric

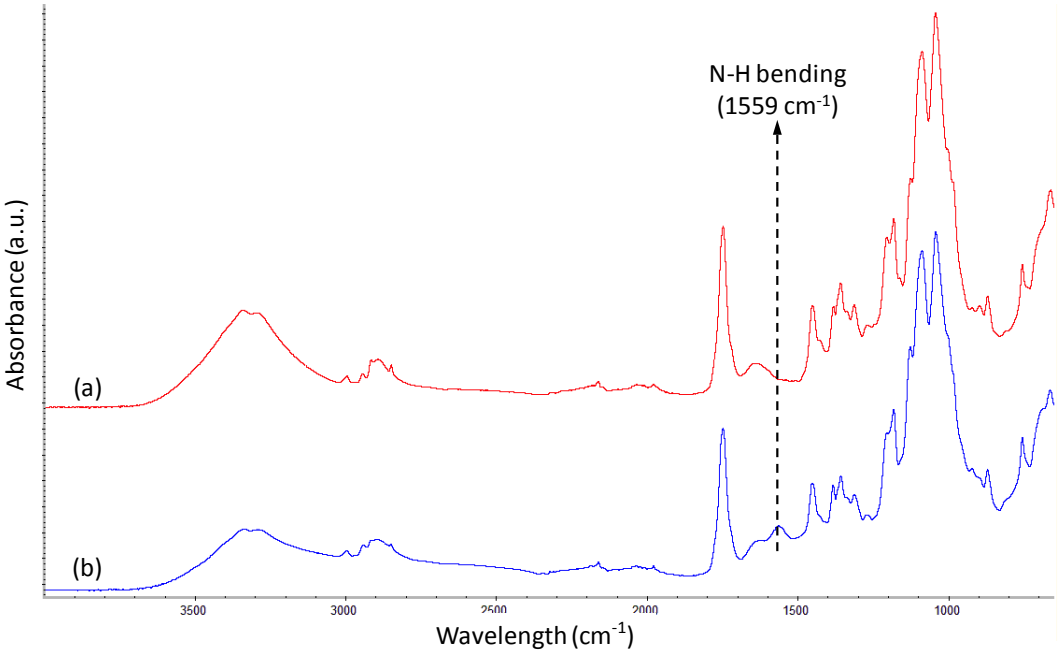

Figure 6.9: IR spectra of (a): untreated and (b): APTES treated flax/PLA fabrics (3 wt-% APTES Sol.)

With the APTES silane treatment, on flax/PLA the intensity of the hydroxyl characteristic peak (3340 cm^{-1}) is reduced, and a new peak at 1559 cm^{-1} due to N-H bending appeared (Figure 6.9). This could be explained by the reaction between the APTES and the reactive hydroxyl

groups on surfaces of flax fibres [12]. APTES can undergo hydrolysis and form the silanol groups to react with hydroxyl groups on the surfaces of flax fibres, thereby leading to the reduction in the intensity of the peak at 3340 cm^{-1} (-OH stretching). The presence of the 1559 cm^{-1} peak (N-H bending) corresponds to amine groups of APTES, in the spectrum of APTES treated flax/PLA (Figure 6.9).

These changes are in fact expected to improve the fibre/matrix interfacial adhesion of flax/PLA composites by the polar-polar bonding between amine groups ($-NH_2$) of the APTES treated flax and the ester groups (-COO-) of PLA. However, this was not the case as the tensile results in Table 6.2 showed that with the use of APTES the tensile properties of flax/PLA laminates decreased. The observation that APTES decreased the fibre/matrix interfacial adhesion of flax/PLA composites is similar to that reported in the literatures where the APTES decreased the interfacial adhesion between glass fibre (hydroxyl rich surfaces) and hydrophilic polymer [12,13]. This was explained by the fact that not only the silanol groups of APTES that could interact with hydroxyl groups on surfaces of the glass fibres, but also the amine functionality due to the high polarity of amine groups ($-NH_2$) of APTES can lead to a formation of hydrogen bonding with hydroxyl groups of glass fibres [13]. Since the surface characteristics of glass and flax fibres are similar in term of hydroxyl rich surfaces, the mechanism of APTES on flax fibres is expected to be similar to that of glass fibres. This therefore leads to a proposed configuration of APTES treated flax fibres where the silanol and amine groups of APTES both interact towards the reactive hydroxyl groups of flax fibres, thereby leaving the propylene sequence of APTES exposed at the surfaces of APTES treated flax, Figure 6.10. This lead to an increase in the hydrophobic character of the APTES treated flax fibres in comparison to the control [12]. As a result of the increase in the hydrophobicity, the compatibility toward PLA matrix of APTES treated flax is therefore decreased and results in a reduction in the fibre/matrix interfacial adhesion of the APTES treated flax/PLA in comparison to the untreated one.

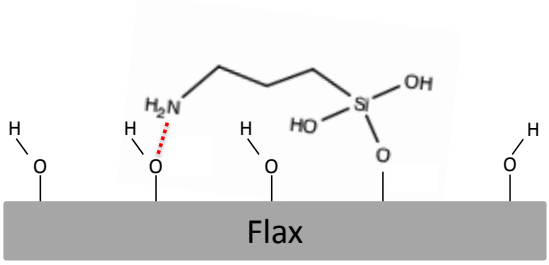

Figure 6.10: The proposed configuration of APTES treated flax fibres

6.2 Optimisation of plasma treatment

Plasma treatment is another technique that has been reported to be used on natural fibre composites in order to improve the fibre/matrix interfacial adhesion [14,15]. The efficiency of plasma treatment depends on type of gaseous and activation energy used for generating plasma flame [16]. The atmospheric argon-plasma was used in this study at 50, 100, and 150

kW intensities to treat flax/PP and flax/PLA fabrics prior to single layered laminate preparation. The tensile properties of the single layered flax/PP and flax/PLA laminates from the plasma treated fabrics were then evaluated to identify the optimised condition of plasma treatment. The stress-strain curves are presented in Figure 6.11 and 6.12, and the results interpreted from the curves are given in Table 6.3.

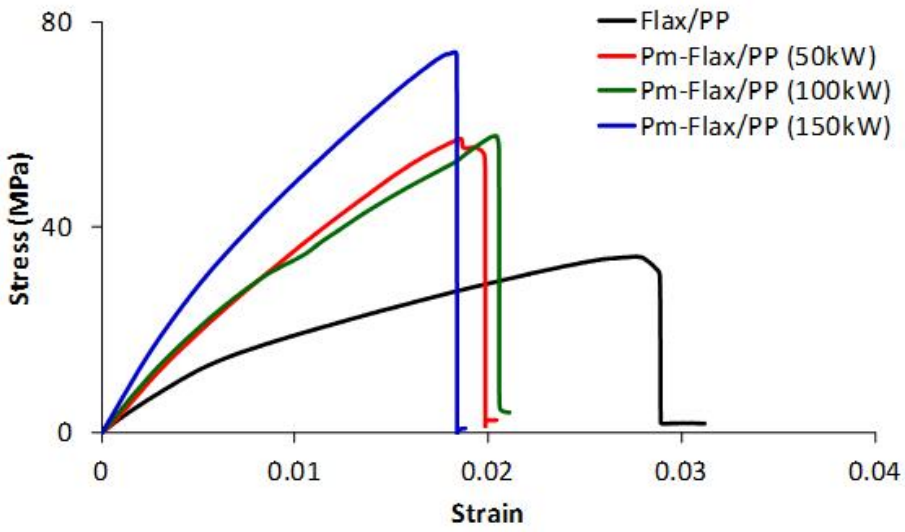

Figure 6.11: Tensile stress-strain curves of flax/PP single layered laminates from the fabrics treated with plasma treatments, with different plasma flame intensities

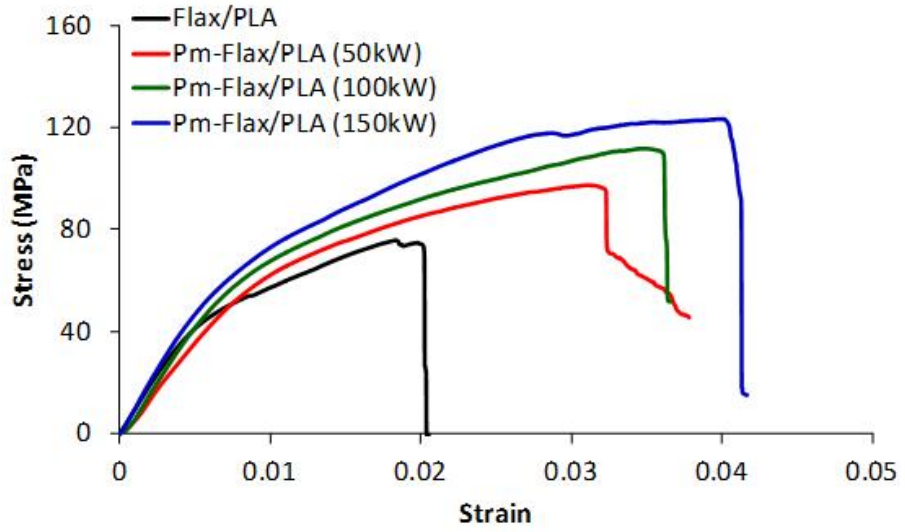

Figure 6.12: Tensile stress-strain curves of flax/PLA single layered laminates from the fabrics treated with plasma treatment at different plasma flame intensities

Table 6.3: Tensile properties of single layered laminates from non-FR fabrics treated with plasma treatment

Sample	Treatment	Tensile Modulus (GPa)	Tensile Strength (MPa)	Strain-at-break (%)
Flax/PP	-	2.9 ±0.4	37 ±5	3.2 ±0.7
Pm-Flax/PP (50kW)	50 kW Plasma	4.1 ±0.3	53 ±6	1.8 ±0.3
Pm-Flax/PP (100kW)	100 kW Plasma	4.4 ±0.1	60 ±6	2.0 ±0.3
Pm-Flax/PP (150kW)	150 kW Plasma	6.3 ±0.1	75 ±2	1.7 ±0.1
Flax/PLA	-	9.0 ±0.7	72 ±6	2.0 ±0.9
Pm-Flax/PLA (50kW)	50 kW Plasma	9.1 ±0.9	100 ±14	3.5 ±0.3
Pm-Flax/PLA (100kW)	100 kW Plasma	10.1 ±0.6	107 ±7	3.1 ±0.8
Pm-Flax/PLA (150kW)	150 kW Plasma	10.7 ±0.5	120 ±5	3.3 ±0.7

6.2.1 Plasma treated flax/PP single layered laminates

The tensile properties of flax/PP single layered laminates increased with the plasma treatment. It can be seen from Table 6.3, the tensile modulus and strength of flax/PP treated with 50 kW plasma flame intensity were higher than the control sample by about 40%. Moreover, the effect of plasma treatment was more pronounced with the higher plasma flame intensity and it can be seen that the tensile properties of flax/PP laminates prepared from the fabric treated with 150 kW plasma flame intensity were much higher than other plasma treated flax/PP samples.

To understand the mechanism of action of plasma on the improvement in tensile properties of flax/PP laminates the surface characteristic of flax/PP fabric before and after plasma treatment characterised by IR are given in Figure 6.13.

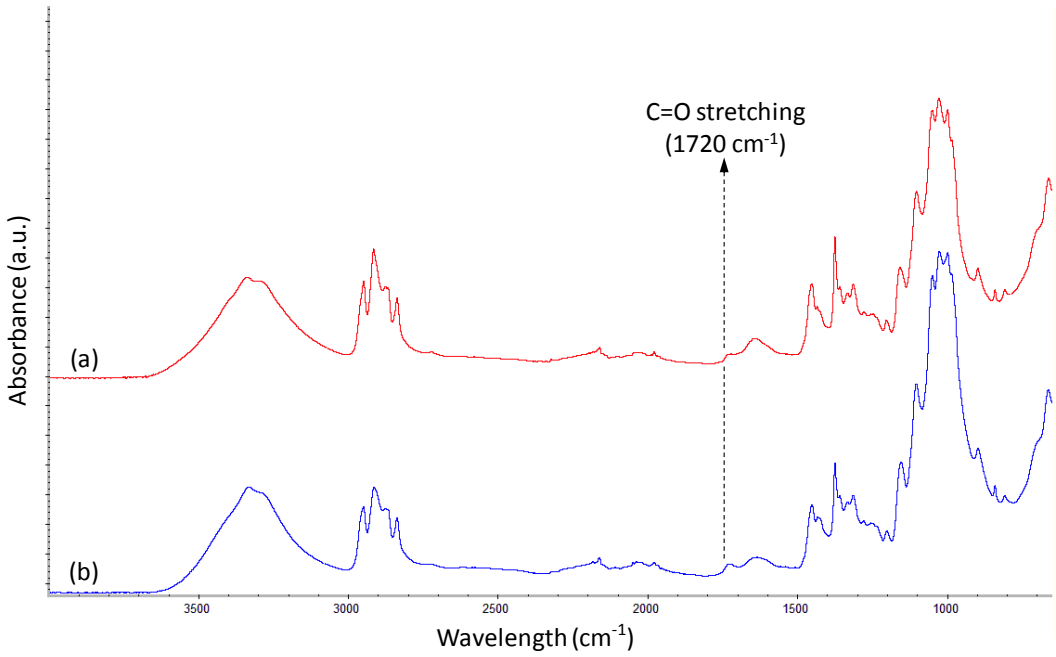

Figure 6.13: IR spectra of (a): untreated and (b): plasma treated flax/PP fabrics

On comparing the IR spectra of control and plasma treated flax/PP, the results show there are small changes in surface chemistry of flax/PP fabric after exposure to plasma flame. It can be seen from Figure 6.13 that only small change in the intensity of the peak at 1720 cm^{-1} (C=O stretching) is observed. In general the plasma could create chemical changes on the surfaces of substrates by creating reactive species and/or functional groups on their surfaces [17]. In flax fibres, the surfaces have highly functional hydroxyl groups, and hence the effect of plasma in modifying its surface chemistry would be less expected compared to PP which has inert surfaces, being a non-polar polymer. Therefore, only the surface chemistry of PP after plasma exposure is expected to be changed. The atmospheric plasma could create the oxygen containing functional groups, i.e. carbonyl group, on the surface of PP by oxidation process [18]. The proposed mechanism of plasma induced oxidation of PP is given in Figure 6.14. The high energy of plasma flame could activate the free radical formation at the tertiary carbon on the polymer backbone of PP. With the presence of oxygen in atmosphere, the produced free radical is oxidised, and forms peroxide group. Due to the low stability of the peroxide, the covalent bond between oxygen atoms breaks down to form radicals, and then influences further chain scission reactions on the polymer chain of PP. This results in the formation of carbonyl group at the end of one broken chain, Figure 6.14. However, on comparing with other functional groups present on the flax/PP fabric, the production of the carbonyl groups could possibly be minor, and hence the intensity of its IR peak at 1720 cm^{-1} (C=O stretching) is low, and could not be seen clearly, Figure 6.13. This mechanism, the formation of carbonyl groups in the structure of plasma treated PP could therefore modify the surface characteristic of PP to become more hydrophilic, and hence has better compatibility with flax fibres as can be seen by the increase in tensile properties of plasma treated flax/PP in comparison to the untreated one, Table 6.3.

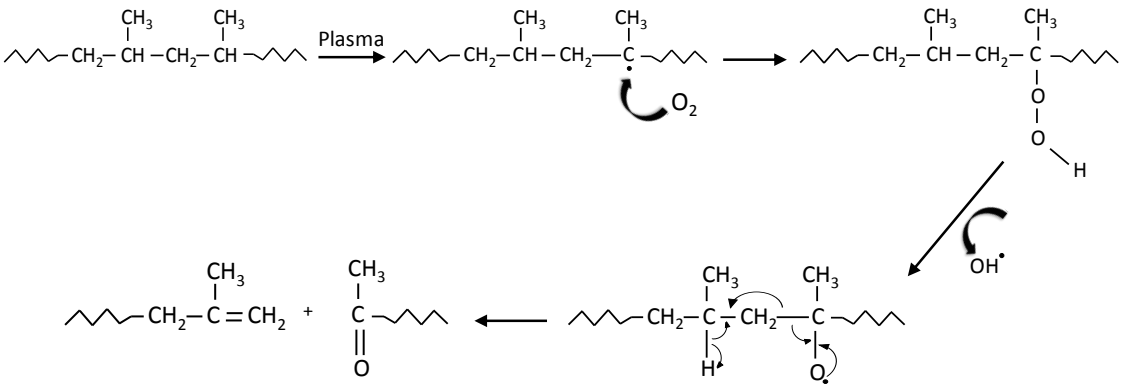

Figure 6.14: The proposed mechanism of plasma treated polypropylene

The surface morphologies of untreated and plasma treated flax/PP fabrics were also observed by scanning electron microscopy (SEM) to have a better understanding of the physical effect of plasma treatment on the fibres surfaces. The SEM micrographs of the fabrics are given in Figure 6.15.

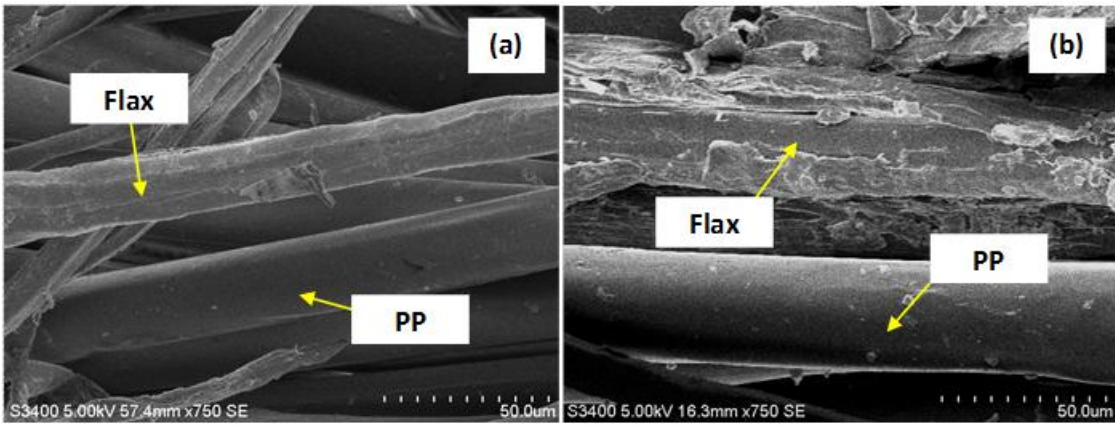

Figure 6.15: SEM images of surface morphology of a) Flax/PP, b) Pm-Flax/PP fabrics

The SEM image of flax/PP fabric shows the surfaces of both flax and PP fibres where the PP fibres have a smoother surface and more uniform diameter in comparison to flax, Figure 6.15 (a). After the plasma treatment, the micrographs show obvious changes in the surface morphology of flax fibres as can be seen from Figure 6.15 (b), which are rougher than that observed in the untreated flax/PP SEM micrograph (Figure 6.15 (a)), the PP surface though is less affected. This could be explained by the etching mechanism of plasma treatment where the ions produced by the plasma flame can bombard and introduce high energy to the surface of the fibres, thereby causing the production of the roughness on the surfaces of the fibres [16,19,20]. This indicates that rather than chemical changes on the surface, the improvement in tensile properties of plasma treated flax/PP in comparison to the untreated one is probably due to the production of rough surfaces on flax fibres which giving rise in sites to perform mechanical interlocking with polymer matrix, and hence resulting in an improvement in mechanical properties of composites [19,20].

6.2.2 Plasma treated flax/PLA single layered laminates

As can be seen from Figure 6.12, the plasma treatment improved the fibre/matrix interfacial adhesion of flax/PLA shown by the increase in tensile properties of plasma treated flax/PLA as compared to the control, Table 6.3. The tensile results showed that with 50 kW plasma treatment the tensile modulus of flax/PLA was slightly increased from 9.0 GPa of the control to 9.1 GPa, and the tensile strength was increased from 72 MPa to 100 MPa. On comparing the effect of different plasma flame intensities, the results show that the efficiency of plasma treatment was greater with the higher plasma flame intensity as can be seen from the tensile modulus and strength of flax/PLA treated with 150 kW plasma flame (10.7 GPa and 120 MPa respectively) were higher than other plasma treated flax/PLA samples, Table 6.3. On comparing the IR spectra of untreated and plasma treated flax/PLA fabrics, similar peaks are observed in both untreated and plasma treated flax/PLA fabrics, Figure 6.16. This could be due to the oxygen related species produced by plasma induced oxidation of PLA, i.e. C-O, -COOH, C=O, have similar IR peaks (mainly at 1720 cm^{-1}) as for the functional groups of flax/PLA fabrics, hence the difference between the IR spectra of plasma treated and untreated flax/PLA could not

be seen [21]. The presence of oxygen in the chemical structure of PLA affecting the chemical modification (oxidation) of PLA caused by plasma treatment is more complex as compared to that proposed for plasma treated PP. However, there is evidence of the increase in the functionalities of PLA after plasma treatment published in literature where X-ray photoelectron spectroscopy (XPS) has been mainly used [21,22]. Jorda-Vilaplana et al [21] have reported that after plasma treatment the functionalities on the surface of PLA was increased due to the formation of peroxide (C-O-O-H), ether (C-O-C), and carbonyl (C=O) functional groups. The presence of these plasma induced functional groups therefore increases the hydrophilicity of PLA, and performs higher fibre/matrix interfacial adhesion with flax fibres in the composite system as seen by the improvement in tensile properties of plasma treated flax/PLA as compared to the control, Table 6.3.

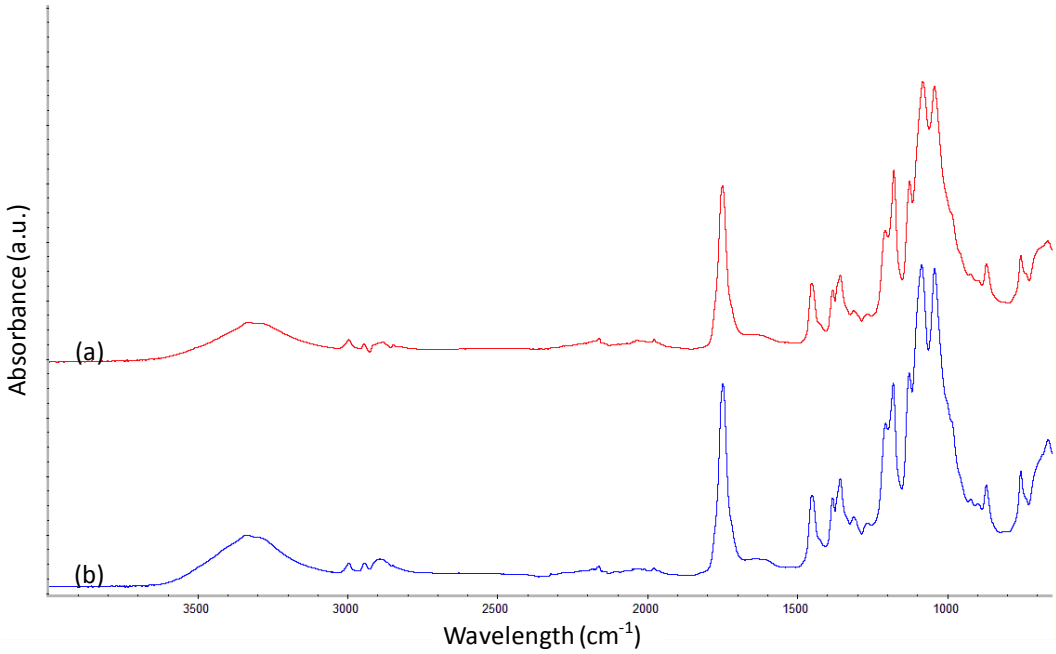

Figure 6.16: IR spectra of (a): untreated and (b): plasma treated flax/PLA fabrics

The SEM micrographs of untreated and plasma treated flax/PLA fabrics are presented in Figure 6.17. The micrographs show that plasma treatment caused a production of rough surface of flax, whereas PLA fibres seem to be less affected. This indicates that besides the chemical effect the plasma could also improve the fibre/matrix interfacial adhesion of flax/PLA by increasing the physical interlocking between fibre and matrix due to the production of rough surface on flax fibres.

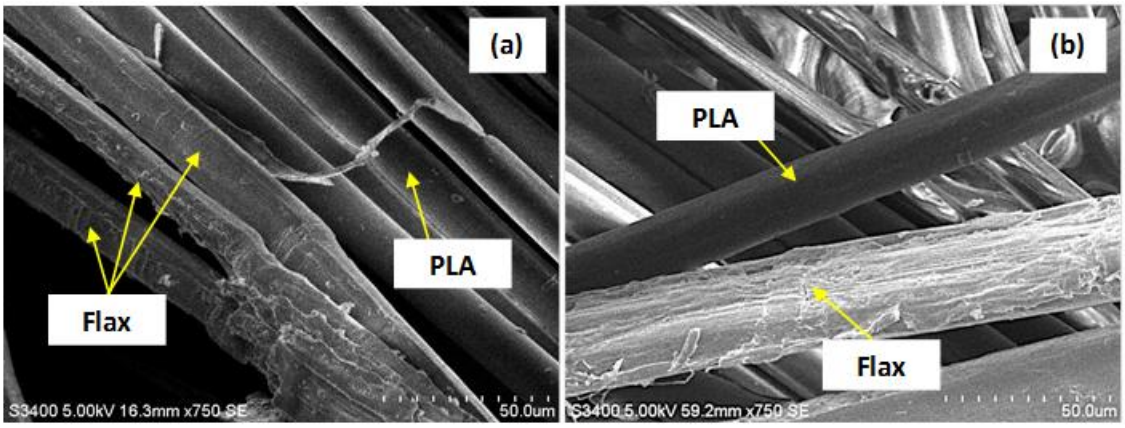

Figure 6.17: SEM images of surface morphology of a) Flax/PLA, b) Pm-Flax/PLA fabrics

6.3 Fibre/matrix interfacial adhesion in FR treated flax/PP and flax/PLA laminates

From the results discussed in *Section 6.1 and 6.2,* it could be seen that both treatments could improve the fibre/matrix interfacial adhesion in flax/PP and flax/PLA composites, except with the use of silane treatment in flax/PLA. The efficiency of these treatments was greater with the use of high concentration of silane solution and strong plasma flame intensity. Therefore, the optimised conditions of 3 wt-% silane solution and 150 kW intensity of plasma flame for silane and plasma treatment, respectively, were chosen for preparing FR treated flax/PP and flax/PLA laminates in order to study their fibre/matrix interfacial adhesion. Although the silane (APTES) treatment of flax/PLA did not improve the fibre/matrix interfacial adhesion of the non-flame retarded flax/PLA (see *Section 6.1.2)*, it was decided to study whether it would show the same effect on flame retarded samples, the FR flax/PLA treated with 3 wt-% APTES solution was also prepared.

Two and eight layered FR treated flax/PP and flax/PLA laminates were prepared from the FR-flax/PP and FR-flax/PLA fabrics treated with different surface modification treatments. To prepare FR treated flax/PP and flax/PLA fabrics, flax/PP and flax/PLA fabrics were treated with guanylurea methylphosphonate (GUP) flame retardant by using the formulation developed in *Chapter 5*. The FR formulation and application was adjusted to obtain 0.9 and 0.6% P on flax/PP and flax/PLA fabrics, respectively. These FR treated fabrics were then treated with silane, plasma, or silane+plasma. Different combinations used are given in Table 6.4. The details of the treated flax/PP and flax/PLA fabrics are given in Table 6.5.

Table 6.4: Sample preparation methods of FR treated flax/PP and flax/PLA fabrics

Method	**The order of fabric treatment**			
	1	**2**	**3**	**4**
FR	FR solution	-	-	-
FR-Si	FR solution	Silane	-	-
FR-Pm	Plasma	FR solution	Plasma	-
FR-Pm-Si	Plasma	FR solution	Plasma	Silane

Table 6.5: Flame retardant flax/PP and flax/PLA fabrics treated with different surface modification treatments

Sample	FR content (%)	P content (%)	Silane content (%)
FR_Flax/PP	10.9	1.0	-
FR-Si_Flax/PP	10.9	1.0	0.6
FR-Pm_Flax/PP	12.2	1.1	-
FR-Pm-Si_Flax/PP	12.2	1.1	1.3
FR_Flax/PLA	7.2	0.6	-
FR-Si_Flax/PLA	7.2	0.6	2.1
FR-Pm_Flax/PLA	9.4	0.8	-
FR-Pm-Si_Flax/PLA	9.4	0.8	3.2

From these treated fabrics, two and eight layered composite laminates were prepared (see *Chapter 3, Section 3.2.5*) for peeling and flexural testing, respectively. In case of two layered composite laminates, since the aim was to prepare specimens for peeling test, a specific sample preparation technique was therefore required. Prior to the melt-pressing step of laminate preparation, the fabrics were therefore partly wrapped with PTFE tape in order to partly bond two layers together, and leave the un-bonded ends for gripping with an Instron Universal tester during the experimental setup of a peeling test as shown in Figure 6.18 (see details in *Section 3.3.4, Chapter 3*).

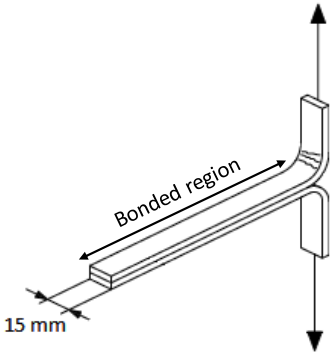

Figure 6.18: A two layered composite laminate for peeling test

6.3.1 Fibre/matrix interfacial adhesion by peeling test

To measure for the fibre/matrix interfacial adhesion by peeling test, the un-bonded ends of the two layered laminates were clamped with the grips of the Instron testing machine. Then the bonded region was peeled off with the Instron at crosshead speed of 50 mm/min (*see Section 3.3.4*). The load (N) and displacement (mm), termed as the peeling force and grip separation distance, were recorded and plotted to a curve as shown in Figure 6.19. The average peeling strength, after disregarding the peeling force of first and last 25 mm of the grip, separation distance was calculated from the curve. The peeling results of control and FR treated flax/PP and flax/PLA laminates are reported in Table 6.6.

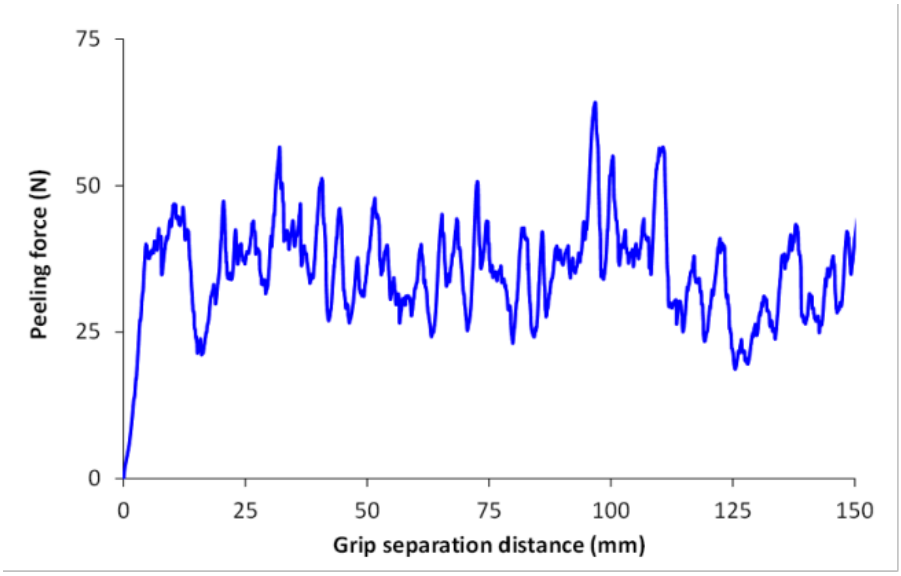

Figure 6.19: Peeling test result of two layered flax/PP laminate

Table 6.6: Peeling test results of FR treated flax/PP and flax/PLA laminates

Sample	Peeling strength (N)	Change in peeling strength* (% w.r.t. Flax/Polym)	Change in peeling strength* (% w.r.t. FR-Flax/Polym)
Flax/PP	35 ±10	-	-
FR_Flax/PP	19 ±6	- 46	-
FR-Si_Flax/PP	24 ±7	- 31	+ 26
FR-Pm_Flax/PP	23 ±7	- 34	+ 21
FR-Pm-Si_Flax/PP	25 ±7	- 29	+ 31
Flax/PLA	50 ±6	-	-
FR_Flax/PLA	35 ±4	- 30	-
FR-Si_Flax/PLA	34 ±3	- 32	- 3
FR-Pm_Flax/PLA	39 ±9	- 22	+ 11
FR-Pm-Si_Flax/PLA	39 ±5	- 22	+ 11

Note: [+] indicates an increase in peeling strength

6.3.1.1 FR treated flax/PP laminates

The results showed that the peeling strength of flax/PP laminate was 35 N. In the presence of guanylurea methylphosphonate (GUP) flame retardant in flax/PP laminate the strength reduced to 19 N, i.e. 46% reduction in comparison to the control. This shows that GUP interferes with the fibre/matrix adhesion of flax/PP, as it is adsorbed onto the surfaces of flax fibre. The IR spectra of untreated and FR treated flax/PP fabrics are presented in Figure 6.20.

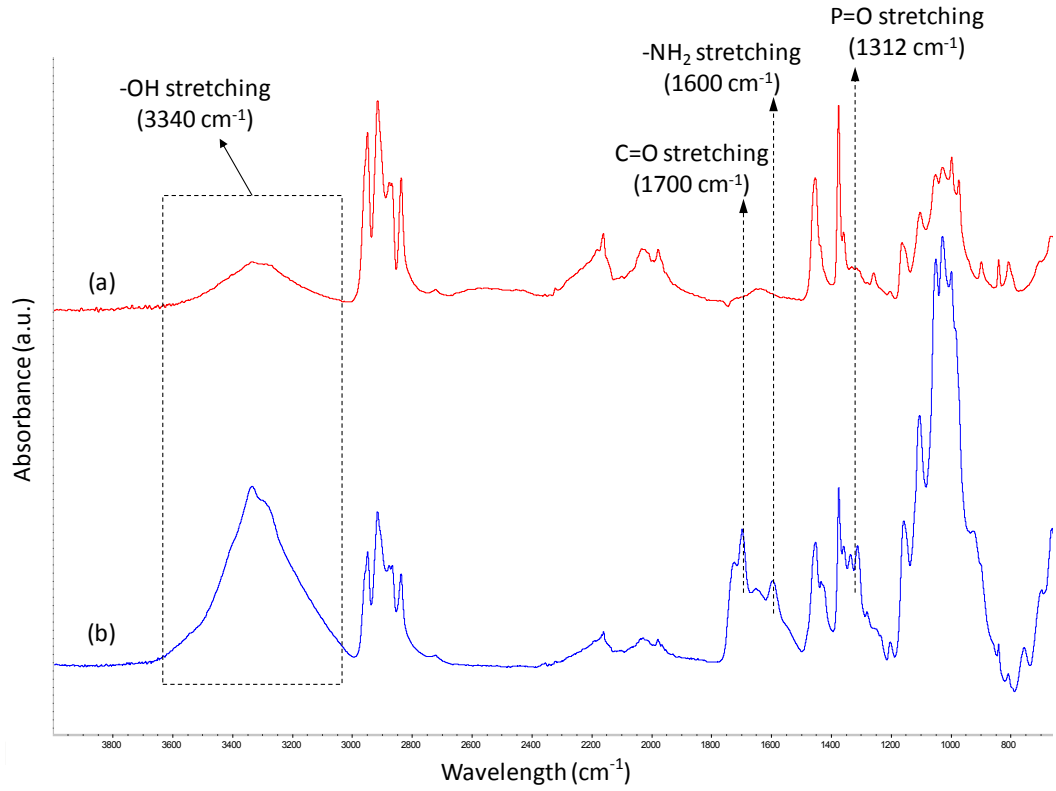

Figure 6.20: IR spectra of (a) untreated and (b) FR treated of flax/PP fabrics

On comparing the IR spectra of untreated and GUP treated flax/PP fabrics, Figure 6.20, the results showed that with the GUP flame retardant treatment the IR peaks of flax/PP were significantly changed, shown by the increase in the intensity of the hydroxyl characteristic peak at 3340 cm^{-1} (-OH stretching), and the appearance of peaks at 1700 cm^{-1} (C=O stretching), 1600 cm^{-1} (-NH_2 stretching) and 1312 cm^{-1} (P=O stretching) [5]. This could be explained by the adsorption of GUP flame retardant on the surfaces of flax fibres in the FR treated flax/PP that lead to the presence of the IR peaks of the functional groups of GUP, Figure 6.21, at 3340 cm^{-1} (-OH stretching) and 1312 cm^{-1} (P=O stretching) corresponding to methylphosphonate moiety, and 1700 cm^{-1} (C=O stretching), 1600 cm^{-1} (-NH_2 stretching) corresponding to guanylurea as shown in the IR spectrum of FR treated flax/PP, Figure 6.20 (b). From this, the surfaces of the FR treated flax therefore become more hydrophilic due to the presence of the functional groups of GUP which is highly polar. As a result of the increase in the hydrophilicity, the compatibility between GUP treated flax and PP is therefore reduced, and results in the decrease in the fibre/matrix interfacial adhesion of flax/PP laminates shown by the reduction in peeling strength of FR treated flax/PP compared to the untreated one, Table 6.6.

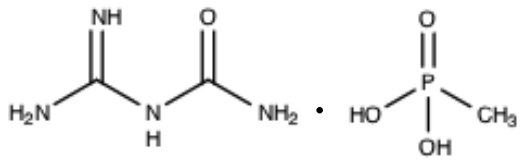

Figure 6.21: Chemical structure of guanylurea methylphosphonate (GUP)

The use of additional surface modification treatments (silane treatment (Si), plasma treatment (Pm), and the combination of both) to prepare FR flax/PP laminates, resulted in a reduction in the peeling strength of FR flax/PP laminates which was less than that of control FR flax/PP, Table 6.6. The results showed that the VTS silane treatment improved the fibre-matrix interfacial adhesion of FR flax/PP as can be seen in the increase in peeling strength from 19 N of FR_Flax/PP laminate to 24 N of FR-Si_Flax/PP and with the plasma treatment, the peeling strength increased to 23 N, Table 6.6. The combination of plasma and silane treatment achieved a peeling strength of 25 N. This shows that the use of the combination of silane and plasma treatments demonstrated only minimal improvement compared to the use of either silane or plasma treatment only. This suggests that the improvement in FR-Pm-Si_Flax/PP was not from the combined effect of plasma and VTS silane on the fibre/matrix interfacial adhesion of FR flax/PP, but possibly because of the increase in the VTS content in the laminate, Table 6.5. Since the fabric preparation process of FR-Pm-Si_Flax/PP was to treat the FR flax/PP fabrics with plasma flame prior to VTS silane treatment, Table 6.4, the plasma improved the wet-pickup ability of the fabric, and hence leading to an increase of VTS content on the fabric after silane treatment. As a result of the increased VTS content, greater reaction between VTS and hydroxyl groups on the surfaces of flax fibres could take place leading to larger reduction in the amount of hydroxyl groups on the surfaces of flax, Figure 6.22; as well as increase in the vinyl groups of VTS on the surfaces of flax fibres to form more siloxane bridges between phases of flax and PP, thereby enhancing the efficiency to improve the fibre/matrix interfacial adhesion of FR flax/PP laminates.

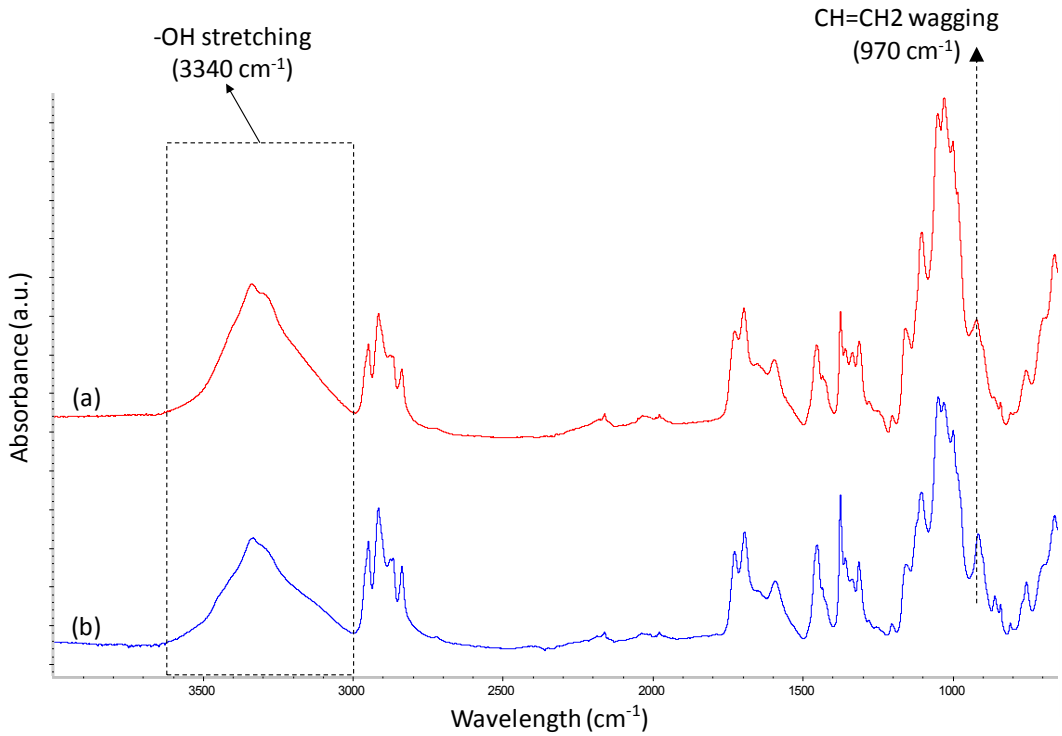

Figure 6.22: IR spectra of (a) FR-Si_Flax/PP and (b) FR-Pm-Si_Flax/PP fabrics

6.3.1.2 FR treated flax/PLA laminates

The peeling results in Table 6.6 show that flax/PLA has peeling strength of 50 N which is much higher than that of flax/PP (35 N). This is due to the chemical structure of PLA, which contains ester groups (-COO-) in its polymer backbone (Figure 6.23), which has a better compatibility with hydroxyl groups on the surface of flax fibres, and hence higher fibre/matrix interfacial adhesion properties compared to PP matrix which is a non-polar polymer.

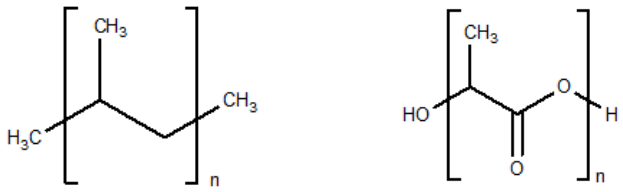

Figure 6.23: Chemical structures of (a): polypropylene (PP) and (b): polylactic acid (PLA)

The GUP flame retardant treatment results show the peeling strength of flax/PLA was reduced by about 30% from 50 N of Flax/PLA to 35 N of FR_Flax/PLA. Similar to that of flax/PP samples, this can be explained by the reaction between flax fibre and GUP flame retardant in the FR treated fabric.

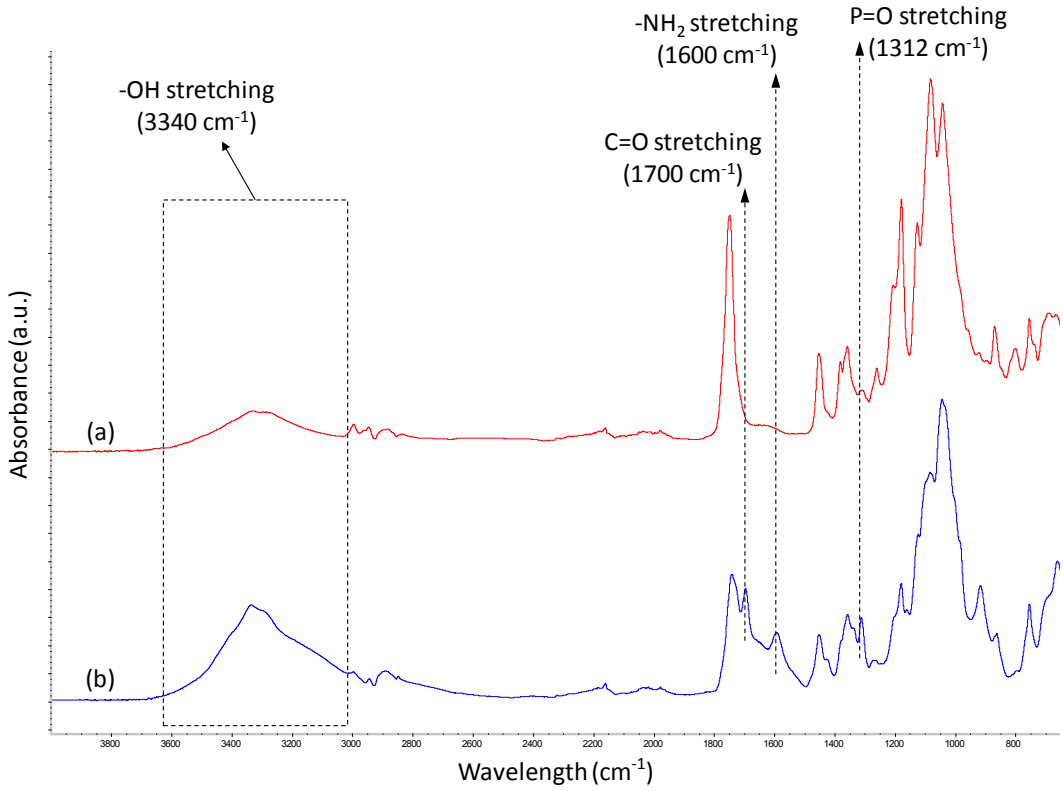

Figure 6.24: IR spectra of (a) untreated and (b) FR treated of flax/PLA fabrics

From Figure 6.24, the IR spectra of untreated and FR treated flax/PLA show that with the addition of GUP flame retardant the surface chemistry of flax/PLA becomes more hydrophilic

which is shown by the presence of IR peaks of polar functional groups of GUP flame retardant at 3340 cm^{-1} (-OH stretching), 1700 cm^{-1} (C=O stretching), 1600 cm^{-1} (-NH_2 stretching) and 1312 cm^{-1} (P=O stretching) in the IR spectrum of FR treated flax/PLA compared to the untreated one. This therefore leads to the decrease in the fibre/matrix interfacial adhesion of flax/PLA laminates; as can be seen in the reduction of the peeling strength of FR treated flax/PLA laminate compared to the control, Table 6.6. The effect of surface modification treatments on the peeling results can be seen in Table 6.6 and show that APTES silane treatment did not show a clear effect on the fibre/matrix interfacial adhesion of FR flax/PLA, as the peeling strengths of FR-Si_Flax/PLA and FR_Flax/PLA were similar. This was as expected as it can be seen from the tensile results of the single layered plasma treated flax/PLA laminates, *Section 6.1,* that the application of APTES silane did not improve the fibre/matrix interfacial adhesion of flax/PLA laminates. However, with the plasma treatment the fibre/matrix interfacial adhesion of FR flax/PLA was improved. The results showed that plasma treatment could increase the peeling strength of FR flax/PLA laminate from 35 N in FR_Flax/PLA to 39 N in FR-Pm_Flax/PLA. The plasma works by an etching mechanism, discussed in *Section 6.2*. Since APTES did not show an effect on fibre/matrix interfacial adhesion of FR treated flax/PLA, the improvement in the peeling strength of FR flax/PLA treated with the combination of APTES silane and plasma treatments was only from the effect of plasma, and as can be seen that the peeling strength is similar to that observed in FR-Pm_Flax/PLA (39 N).

6.3.2 Fibre/matrix interfacial adhesion by flexural test

The fibre/matrix interfacial adhesion of eight layered laminates from the FR-flax/PP and FR-flax/PLA fabrics treated with different surface modifications (see Table 6.5) were also investigated by using flexural test. The flexural modulus and flexural strength results of these laminates are given in Table 6.7.

Table 6.7: Flexural properties of FR treated flax/PP and flax/PLA laminates

Sample	Flexural modulus (GPa)	Flexural strength (MPa)
FR_Flax/PP	8.3 ±0.6	71 ±4
FR-Si_Flax/PP	9.7 ±1.7	61 ±4
FR-Pm_Flax/PP	9.9 ±0.7	64 ±9
FR-Pm-Si_Flax/PP	11.0 ±1.4	84 ±10
FR_Flax/PLA	13.7 ±1.0	121 ±6
FR-Si_Flax/PLA	13.7 ±0.2	115 ±11
FR-Pm_Flax/PLA	17.5 ±0.2	137 ±1
FR-Pm-Si_Flax/PLA	17.1 ±1.1	118 ±1

Note: Fibre volume fractions in all flax/PP samples are ~ 40%, for all flax/PLA samples are ~ 60%

6.3.2.1 FR treated flax/PP laminates

The effect of surface modification treatments on the flexural properties of the FR treated flax/PP laminates is similar to that by peeling test. As can be seen from Table 6.7, the flexural properties, in particular flexural modulus, of FR treated flax/PP were improved with the use of surface modification treatments. The flexural modulus of FR treated flax/PP laminate increased from 8.3 GPa to 9.7 GPa and 9.9 GPa with the VTS silane and plasma treatments, respectively. With the combination of silane and plasma treatments the flexural modulus of FR treated flax/PP was improved to 11.0 GPa which was the highest compared to other FR treated flax/PP samples, Table 6.7.

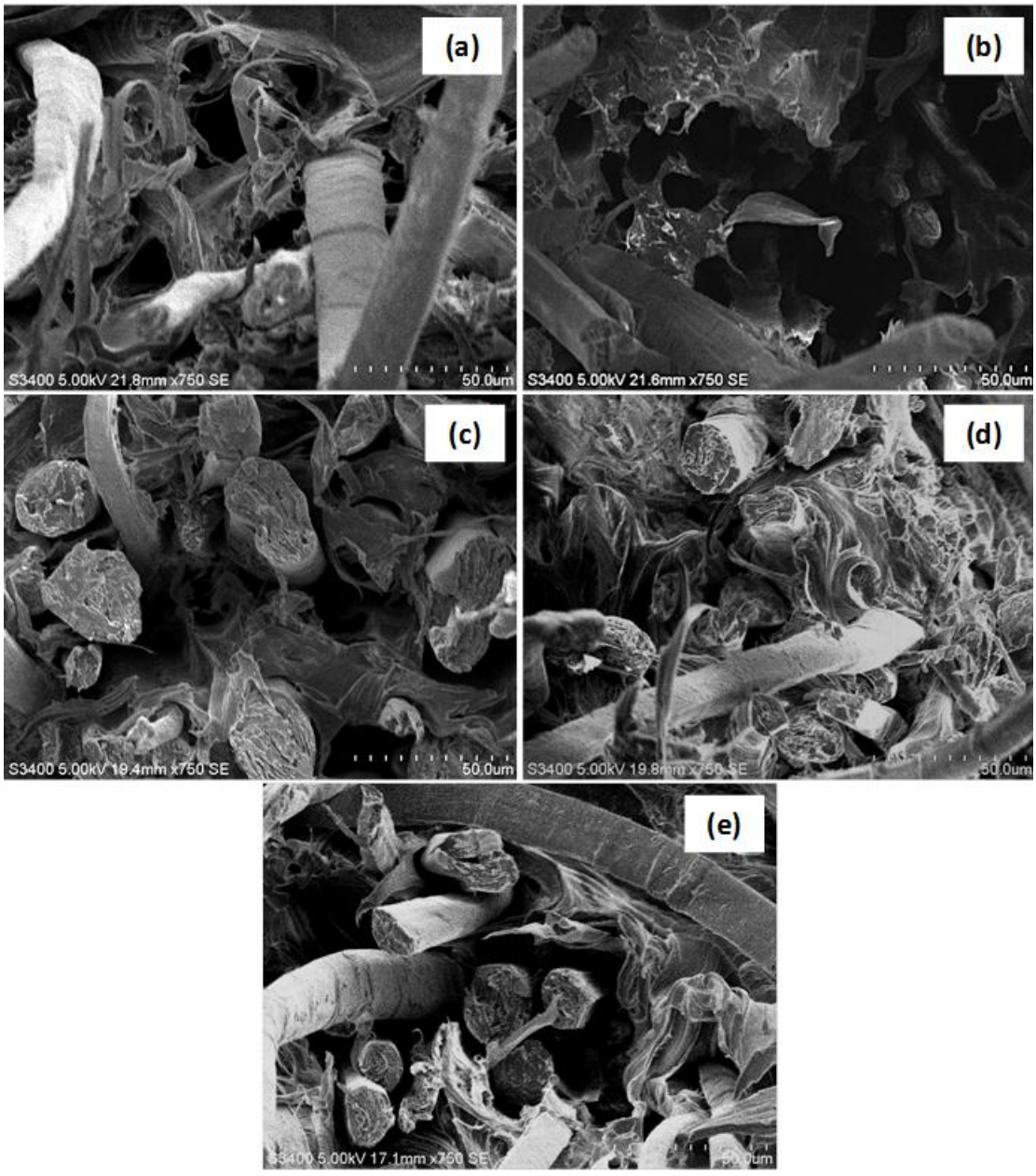

Figure 6.25: SEM images of the fracture surfaces of (a) Flax/PP, (b) FR_Flax-PP, (c) FR-Si_Flax/PP, (d) FR-Pm_Flax/PP, and (e) FR-Pm-Si_Flax/PP laminates

To support the discussion that the surface modification treatments could improve the fibre/matrix interfacial adhesion of FR treated flax/PP composites, the fractured surfaces of the FR treated flax/PP laminates after flexural bending test were observed by using scanning electron microscopy (SEM), Figure 6.25. As seen in Figure 6.25 (a) and (b), the fractured surfaces of control and FR treated flax/PP laminates without any surface modification treatments show that flax fibres have been pulled-out from the polymer matrix before breaking, indicating the weak interfacial adhesion between fibres and polymer matrix. Whereas, with the use of surface treatments the improvement in fibre/matrix interfacial adhesion is clearly observed as that the fibre breaking positions of FR-Si_Flax/PP, FR-Pm_Flax/PP and FR-Pm-Si_Flax/PP laminates are at similar level as the fractured surfaces of PP matrix [23,24].

6.3.2.2 FR treated flax/PLA laminates

On comparing the flexural properties of FR flax/PLA treated with different surface treatments, the results showed a similar trend as observed in peeling test. From Table 6.7, the results show that APTES silane did not have much effect on the flexural properties of FR treated flax/PLA shown by the similar flexural modulus for FR_Flax/PLA and FR-Si_Flax/PLA samples. On the other hand, plasma treatment significantly improved the flexural properties, in particular flexural modulus. The flexural modulus of FR treated flax/PLA was increased by about 28% from 13.7 GPa in FR_Flax/PLA to 17.5 GPa in FR-Pm_Flax/PLA. The combination of silane and plasma treatments produced similar effect to that observed in the peeling test. The results show that silane reduced the effect of plasma treatment which can be seen in the reduction of the flexural modulus and strength of FR-Pm-Si_Flax/PLA which is lower than that of FR-Pm_Flax/PLA, Table 6.7. These results are also supported by the SEM micrographs of the fractured surfaces of FR-flax/PLA treated with different surface modification treatments as shown in Figure 6.26. The APTES treatment did not show a clear effect on fibre/matrix interfacial adhesion properties of FR treated flax/PLA as traces of fibre-pulled out can be clearly seen in the fractured surfaces of both FR_Flax/PLA and FR-Si_Flax/PLA, Figure 6.26 (b) and (c). In contrast, with the effect of plasma treatment the fibre/matrix interfacial adhesion of FR-Pm_Flax/PLA and FR-Pm-Si_Flax/PLA was significantly improved in comparison to the untreated one (FR-Flax/PLA). This can be seen from the breaking positions of flax fibres of FR-Pm_Flax/PLA and FR-Pm-Si_Flax/PLA which are at the same level as PLA polymer matrix, Figure 6.26 (d) and (e). These therefore lead to the conclusion that to achieve the maximum improvement of fibre/matrix interfacial adhesion of FR-flax/PLA, only plasma treatment is required.

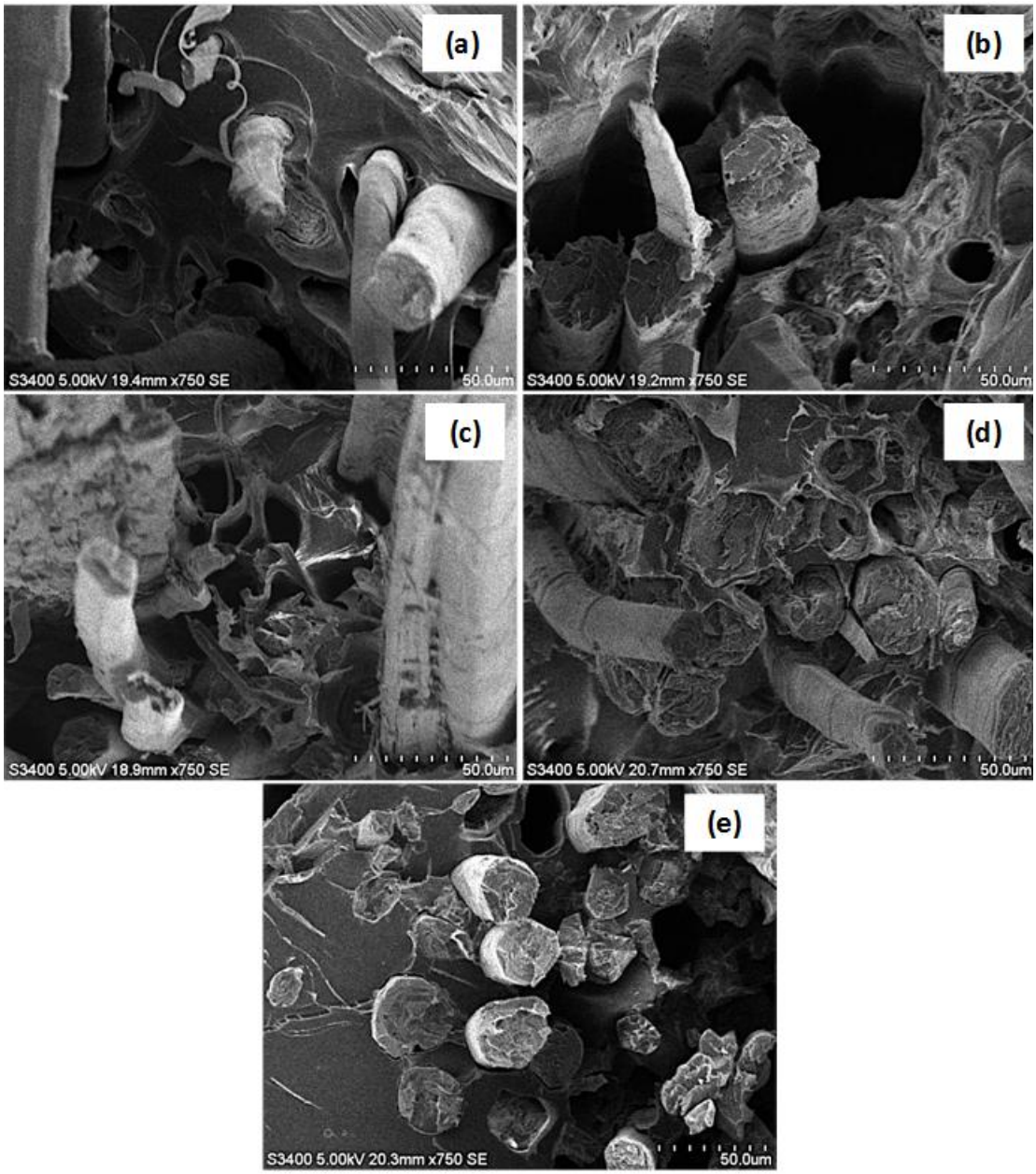

Figure 6.26: SEM images of the fracture surfaces of (a) Flax/PLA, (b) FR_Flax-PLA, (c) FR-Si_Flax/PLA, (d) FR-Pm_Flax/PLA, and (e) FR-Pm-Si_Flax/PLA laminates

6.4 Conclusions

The flame retardant treatment of flax/PP fabrics reduced the fibre/matrix interfacial adhesion in FR-flax/PP laminates, as observed by the reduction in peeling strength and flexural properties, as compared to the composites without FR treatment. The use of surface modification (silane, plasma and the combination of both) treatments on FR treated flax/PP fabrics demonstrated an improvement in the fibre/matrix interfacial adhesion of FR flax/PP laminates. The maximum improvement was obtained with the combination of silane and plasma treatment as shown by the highest peeling strength and flexural properties in FR-Pm-Si_Flax/PP compared to other flax/PP samples.

For FR treated flax/PLA without surface treatment, the GUP flame retardant also reduced the fibre/matrix interfacial adhesion. The plasma treatment improved the fibre/matrix interfacial adhesion of FR treated flax/PLA, whereas silane showed no effect. Therefore, to obtain the maximum improvement in fibre/matrix interfacial adhesion of FR treated flax/PLA laminates only plasma treatment is required.

6.5 References

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Chapter 7: Development of flame retardant polymer matrices

Since one of the objectives of this work was to develop flame retardant polymer matrices, polylactic acid (PLA) and polypropylene (PP) as thermoplastic (with an aim to eventually extrude into fibres), and poly(furfuryl alcohol) (furan resin) as thermoset matrix materials were chosen. In case of furan resin, although it is inherently non-flammable (see *Chapter 4*), but used in natural fibre composite, the high flammability of natural fibres may make the derived composite flammable. Hence, it is worth developing a flame retardant furan resin, in order to compromise with the high flammability of natural fibres. The content of this chapter is divided in two sections based on type of polymer, thermoplastic (PP and PLA) and thermoset (furan resin). In order to render these polymers flame retardant, different phosphorus (P) based flame retardants were introduced to these polymers by using different techniques depending upon type of the polymer, i.e. melt-compounding for thermoplastic, and mechanical mixing prior to resin casting for thermoset. The fire performance of these flame retardant polymers was studied by using limiting oxygen index (LOI), UL-94 and cone calorimetry in order to identify the most effective flame retardant for a particular polymer matrix to be used. In thermoplastic group, the processability of the developed flame retardant polymers (PP and PLA) to extrude into filaments was also explored to identify the optimised flame retardant formulation for producing flame retardant PP and PLA fibres to be used as part of flax/PP and flax/PLA commingled fabrics.

7.1 Flame retardant polylactic acid (FR-PLA) and polypropylene (FR-PP) polymers/fibres

In order to develop flame retardant PP or PLA fibres the criteria of selection of flame retardants was (i) the flame retardant should be phosphorus based and (ii) particle size of the flame retardant should be ≤ 10 μm or it should melt at the temperature used for fibre extrusion. These criteria were based on a preliminary study where the effect of the incorporation of an organically modified nanoclay (Cloisite C30B, Southern Clays) and ammonium polyphosphate (APP, FR Cros C60, Budenheim) into polylactic acid (PLA) was studied (details given in Appendix I). The results indicated that the nanoclay did not show a clear effect on the flammability of the PLA, while APP significantly reduced its flammability. With the addition of APP to give a 2% P content (6.7 wt-% solid content of APP) in PLA in sample PLA+APP(2%P) and the sample could pass UL-94 test with V-0 rating. However this sample, PLA+APP(2%P) could not be extruded into filaments, hence was discarded.

The selected flame retardants were organic nitrogen-phosphorus compound (NP), organic phosphorus compound (OP), and zinc phosphinate (ZP). NP flame retardant has small particle size of 10 μm, whereas OP and ZP flame retardants melt at 245^{o}C and 200^{o}C respectively, hence these are expected to reduce the problem of flame retardant dispersion in fibre extrusion process, if the extrusion is done at these temperatures.

The selected flame retardants were compounded into the polymers (i.e. PLA and PP) by using a twin screw extruder. During compounding the maximum processing temperature was 225^{o}C in all samples. The concentration of flame retardants were adjusted to obtain 1 and 2 wt-% P contents. The formulations used are given in Table 7.1. The compounding procedure and condition have already been described in details in *Section 3.2.2, Chapter 3*.

Table 7.1: Sample matrix of PLA and PP containing different P based flame retardants

Sample	FR additive	Percent mass content (wt-%)	
		Polymer	Flame retardant
Polym+NP(1%P)	Organic nitrogen-phosphorus compound	92.9	7.1
Polym+OP(1%P)	Organic phosphorus compound	95.8	4.2
Polym+OP(2%P)		91.6	8.4
Polym+ZP(1%P)	Zinc phosphinate	95.0	5.0
Polym+ZP(2%P)		90.0	10.0

Note: PLA containing NP flame retardant at 2 wt-% P level could not be processed as the FR content was very high

Prior to extruding into filaments, the compounded FR-polymers were transformed to 3 mm plaques by melt-pressing at 180^{o}C, and their flammability was studied.

7.1.1 Flame retardant polylactic acid (FR-PLA) polymers/fibres

7.1.1.1 Flammability of flame retardant PLA

The flammability of FR-PLA plaques was investigated by using limiting oxygen index (LOI), UL-94, and cone calorimetry. The LOI and UL-94 results of these FR-PLA samples are given in Table 7.2. The LOI results in Table 7.2 show that PLA has LOI of 18.6%. On addition of NP at 1% P level, the LOI of PLA was increased to 35% which is the highest LOI value compared to other FR-PLA samples. The results of PLA+OP show that OP flame retardant reduced the flammability of PLA by increasing the LOI of PLA from 18.6% to 29.2 and 29.8%, at the 1 and 2% P content of OP in the samples, respectively. This indicates that 1% P level for OP is enough as there is not much increase in the LOI value on further increasing the FR content.

Table 7.2: LOI and UL-94 results of FR-PLA plaques

Sample	LOI	UL-94 horizontal	UL-94 vertical	
	(%)	B. Rate (mm/min)	B. Rate (mm/min)	V-Rate
PLA	18.6	31.5 ±6.9	71.4 ±4.5	Failed
PLA+NP(1%P)	35.0	-*	-*	V-0
PLA+OP(1%P)	29.2	-*	-*	V-0
PLA+OP(2%P)	29.8	-*	-*	V-0
PLA+ZP(1%P)	21.2	-**	-**	V-2
PLA+ZP(2%P)	22.6	-**	-**	V-2

* Sample did not ignite

** The flame went out with burning drips soon after removal of the flame

With ZP flame retardant, the results show that at 1% P level the LOI increased to 21.2%, which further increased to 22.6% with 2% P level. These values are though much lower than those containing NP or OP samples. In UL-94 test, the results show that PLA failed the vertical rating test as the sample completely burned up to the sample holder with the rate of burning of 71 mm/min. The addition of NP at 1% P level improved the fire performance of PLA to prevent the sample from ignition in UL-94 test, hence V-0 rating could be achieved. This is as expected due to the significant improvement in the LOI value of PLA+NP(1%P) compared to the control, Table 7.2. As the sample did not ignite, the vertical and horizontal rate of burning of PLA+NP(1%P) could not be measured. In case of OP flame retardant, (PLA+OP) at both 1 and 2% P levels with the LOI of 29 - 30% could also pass V-0 rating. This shows that 1% P level of OP flame retardant is enough to pass V-0. On the other hand, with the lower LOI values of PLA containing ZP flame retardant compared to others (Table 7.2), they only achieved V-2 rating as the melt-flaming dripping caused the ignition of the cotton underneath the specimen during the UL-94 vertical test. The rate of burning of PLA+ZP samples could not be measured, as the flame went out with the flaming drops soon after removal of the burner.

The effect of these flame retardants on the flammability of PLA was also studied by using cone calorimetry at 35 kW/m^2 external heat flux. The results of heat release rate (HRR), rate of smoke release (RSR), and mass loss as a function of time are presented in Figure 7.1 respectively. The results interpreted from these curves are given in Table 7.3

Table 7.3: Cone calorimetric results and fire rating parameters of FR-PLA plaques at 35 kW/m^2

Sample	TTI (s)	t_{PHRR} (s)	PHRR (kW/m^2)	THR (MJ/m^2)	EHC (MJ/kg)	TSR (L)	Yield (%)	Fire rating parameters	
								FPI (s/(kW/m^2))	FIGRA (kW/m^2· s)
PLA	64 ±3	163 ±4	537 ±6	66 ±1	17 ±1	7 ±3	1.2 ±0.7	0.12 ±0.01	3.9 ±0.4
PLA+NP(1%P)	124 ±5	154 ±4	668 ±26	37 ±3	12 ±1	482 ±62	3.5 ±0.9	0.19 ±0.01	4.2 ±0.2
PLA+OP(1%P)	87 ±3	161 ±4	661 ±20	56 ±1	16 ±1	140 ±26	1.3 ±0.8	0.13 ±0.01	4.1 ±0.4
PLA+OP(2%P)	106 ±2	168 ±21	634 ±22	53 ±2	14 ±1	171 ±1	3.9 ±1.8	0.17 ±0.01	4.0 ±0.5
PLA+ZP(1%P)	50 ±2	119 ±2	715 ±11	54 ±1	18 ±1	105 ±9	5.2 ±1.8	0.07 ±0.01	6.0 ±0.1
PLA+ZP(2%P)	45 ±4	114 ±7	659 ±26	53 ±3	18 ±1	140 ±7	6.4 ±1.5	0.07 ±0.01	5.8 ±0.1

The results in Figure 7.1 and Table 7.3 show that PLA ignited at 64 s, and burned with 537 kW/m^2 of peak of heat release rate (PHRR) producing 66 MJ/m^2 of total heat release (THR). At the end of combustion, PLA produced 1.2% of charred residue. On addition of NP flame retardant at 1% P level, the results show significant improvement in the time-to-ignition (TTI) as can be seen that the TTI of PLA was increased from 64 s of the control to 124 s in PLA+NP(1%P). PLA+NP(1%P) however shows higher PHRR of 668 kW/m^2 as compared to 537 kW/m^2 in control sample, but burned for a shorter time (Figure 7.1 (a)) hence produced less THR (37 MJ/m^2). NP flame retardant at 1% P content also shows slight improvement in the char formation, i.e. 3.5% as compared to 1.2% in the control.

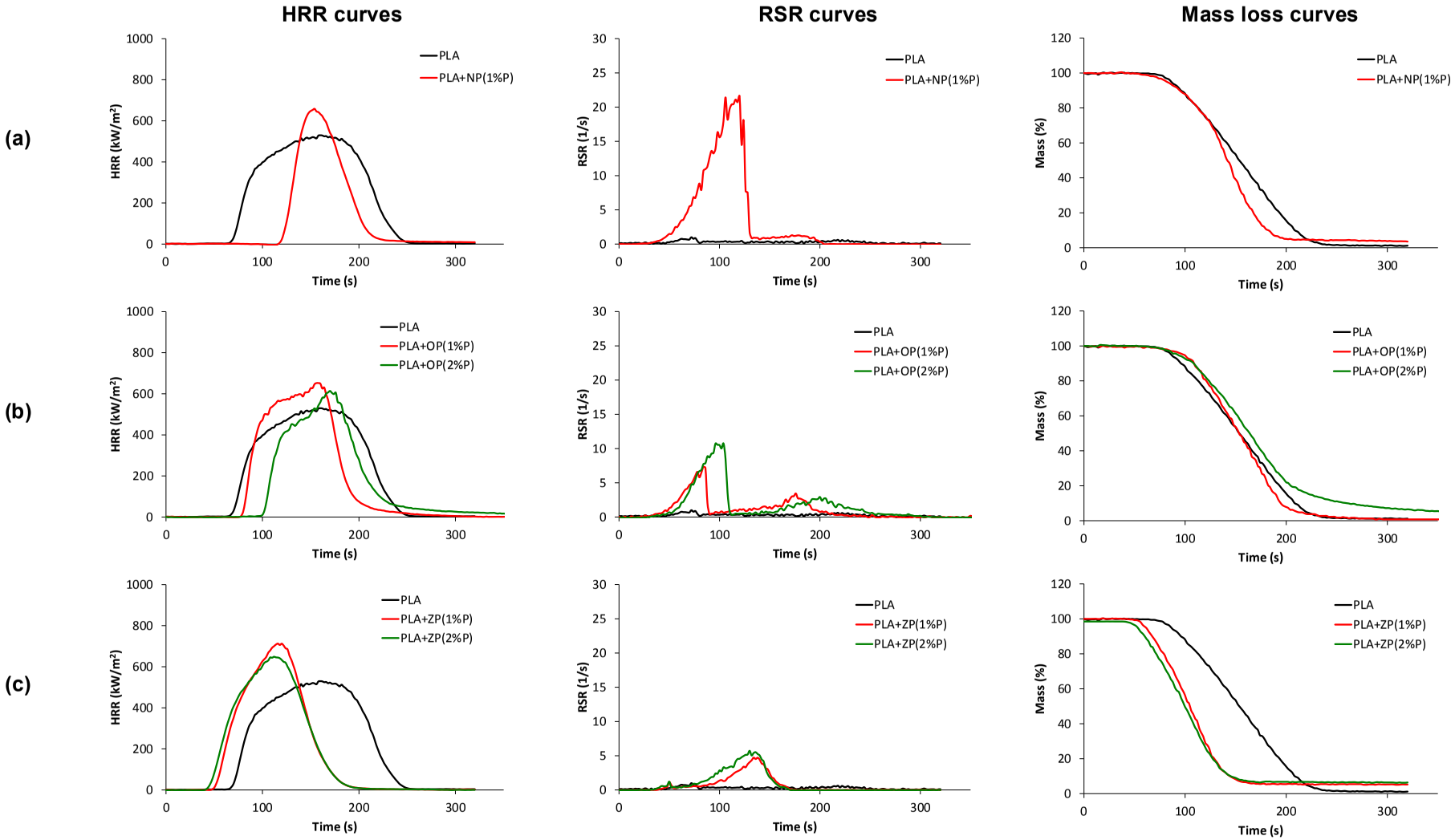

Figure 7.1: HRR, RSR and mass loss curves as a function of time of PLA containing (a) NP, (b) OP, and (c) ZP flame retardants at 35 kW/m^2

The OP flame retardant at 1% P level (PLA+OP(1%P)) increased the TTI to 87 s, but produced 661 kW/m^2 PHRR. However, due to the shorter burning time of PLA+OP(1%P), it produced lower THR of 56 MJ/m^2 in comparison to 66 MJ/m^2 of the control. The charred residue of PLA+OP(1%P) is similar to that of the control. On increasing OP content (2% P level), the TTI was increased to 106 s, whereas PHRR and THR were reduced to 634 kW/m^2 and 53 MJ/m^2, the PHRR though is still higher than that of the control PLA. On increasing the OP content to 2% P level, the char formation of the sample was also improved (3.9%). In contrast, the presence of ZP at 1% P level reduced the TTI of PLA from 64 s in the control to 50 s, and increased the PHRR from 537 kW/m^2 to 715 kW/m^2. Although PLA+ZP(1%P) burned with higher PHRR than the control, it burned for a shorter time (Figure 7.1 (c)), thereby produced lower 54 MJ/m^2 THR. ZP flame retardant significantly improved the char formation (5.2%). With the increased amount of ZP, the TTI of PLA was further decreased to 45 s in PLA+ZP(2%P), and the PHRR reduced from 715 kW/m^2 in PLA+ZP(1%P) to 659 kW/m^2 in PLA+ZP(2%P). PLA+ZP(2%P) shows similar THR as observed in PLA+ZP(1%P), but produced higher amount of charred residue of 6.4% in comparison to 5.2% in PLA+ZP(1%P).

On comparing the effective heat of combustion, which is a quantitative measurement of heat produced by combustion of a unit quantity of material, in these flame retardant PLA samples, the addition of NP at 1% P level improved the fire performance of PLA by reducing the EHC of PLA from 17 MJ/kg to 12 MJ/kg. For OP flame retardant, the results show that it also reduced the EHC of PLA, but its performance was less in comparison to the NP flame retardant, as the EHC of PLA was decreased to 16 MJ/kg and 14 MJ/kg with 1 and 2% P level, respectively. On the other hand, ZP flame retardant shows negative effect as it slightly increased the EHC of PLA from 17 MJ/kg to 18 MJ/kg.

Two other fire parameters that can be used to rank the fire safety of materials are the fire performance index (FPI) and the fire growth rate (FIGRA). FPI is defined as a ratio of the time-to-ignition (TTI) to the peak of heat release rate (PHRR). There is a correlation of FPI to the time to flashover as a lower FPI value suggests an accelerated flashover event [1], in other words the higher the value, the safer it is. The FPI results in Table 7.3 show that the addition of NP improved the fire performance of PLA by increasing the FPI from 0.12 s/(kW/m^2) in the control to 0.19 s/(kW/m^2) in PLA+NP(1%P). With OP flame retardant, the FPI of PLA was also increased to 0.13 s/(kW/m^2) and 0.17 s/(kW/m^2) in PLA+OP samples at 1 and 2% P content, respectively. In contrast, the negative effect is seen in PLA+ZP samples as the presence of ZP decreased the FPI of PLA to 0.07 s/(kW/m^2) at both 1 and 2% P content. These FPI results show the same trend as observed in EHC as only NP and OP flame retardants improved the fire safety of PLA as shown by the increase in the FPI values as compared to the control, whereas ZP flame retardant shows negative effect by reducing the FPI of PLA. FIGRA (fire growth rate = maximum quotient of HRR *(t)/* T_{PHRR}, which often equals to PHRR/ T_{PHRR}) in a cone calorimeter [2], if the peak is sharp and the gradient is well defined, indicating the burning propensity of a material. Lower the FIGRA value, lower the fire growth in a material. The results in Table 7.3

show that the addition of NP and OP flame retardants show marginal effect on the FIGRA of PLA as can be seen from the similar FIGRA values in PLA+NP(1%P) (4.2 kW/m^2·s) and PLA+OP (4.1 and 4.0 kW/m^2·s at 1 and 2% P content, respectively), as compared to the control (3.9 kW/m^2·s). This is due to the reason that NP and OP flame retardants although increased TTI of PLA, they also caused the samples to burn with higher PHRR than the control. In contrast, ZP flame retardant shows negative effect and reduces the fire safety rating of PLA similar to that observed in FPI results as ZP increased the FIGRA of PLA to 6.0 and 5.8 kW/m^2·s at 1 and 2% P content, respectively.

The relative overall fire performances of these FR-PLA samples were also evaluated to assess the fire hazard of the samples by plotting the total heat release (THR) against the fire growth rate values, calculated by dividing PHRR by TTI [1,3], as presented in Figure 7.2. Fire safe materials should have low THR and fire growth rate value (PHRR/TTI), hence the samples with the high fire safety should fall close to the coordinates (0,0) on the 2-D plot [1]. The results from Figure 7.2 show that although PLA containing ZP flame retardant samples show lower THR than the control, their fire growth rating are much higher, hence having relative low fire safety rating as compared to the control. In contrast, the samples containing NP and OP flame retardants show superior fire safety rating, as can be seen from their lower THRs and fire growth rating values in comparison to the control, where the PLA+NP(1%P) shows highest fire safety rating with the lowest THR and fire growth rate value, followed by PLA+OP(2%P) and PLA+OP(1%P), respectively. These results are as expected from the UL-94 vertical test in that only these samples could pass V-0 rating, Table 7.2.

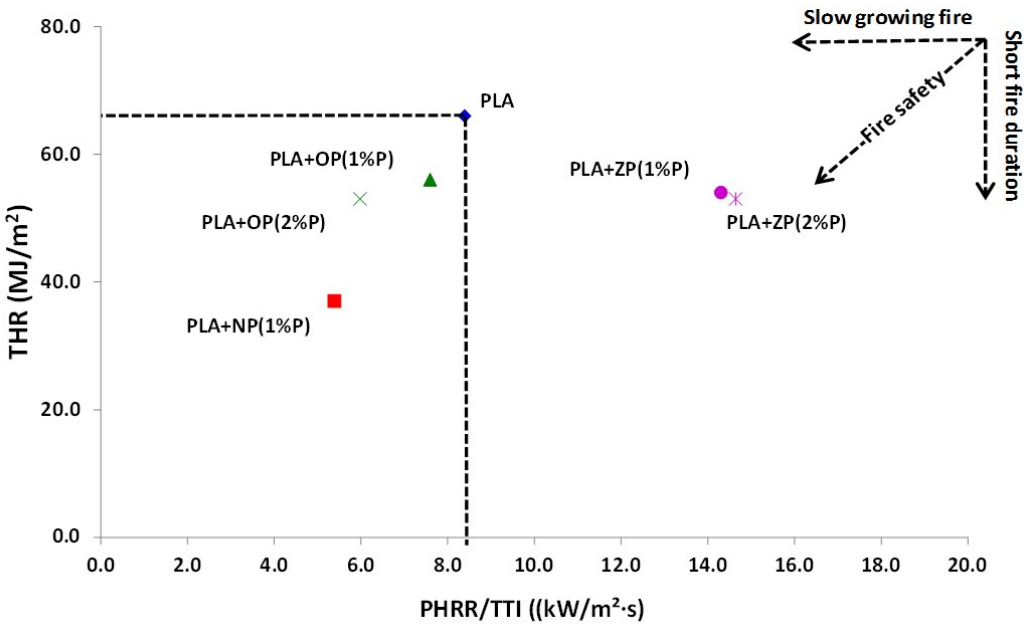

Figure 7.2: 2-D fire safety index of PLA containing different P based flame retardants exposed to 35 kW/m^2 heat flux

These cone calorimetric results show that NP and OP flame retardants improved the fire retardancy of PLA by both reducing the flammability (i.e. increase in TTI, and reduction in the THR and EHC) and increasing the fire safety rating. Whereas, ZP flame retardant although reduced THR, it did not improve the fire safety rating of the PLA. Hence, only NP and OP flame retardants were selected as the most effective flame retardants for PLA polymer, and taken forward to produce the FR-PLA fibres.

7.1.1.2 Thermal decomposition of flame retardant PLA

To understand the difference in the fire performance of these FR-PLA samples by different tests, it is important to understand how these flame retardants work. The thermal decompositions of the FR-PLA were therefore investigated by using thermogravimetric analysis (TGA) under air and nitrogen atmospheres from room temperature to 700^{o}C. The TGA, derivative thermogravimetric analysis (DTG), and differential temperature analysis (DTA) curves of selected samples are graphically presented in Figure 7.3 and 7.4, whereas the derived data for all samples are reported in Tables 7.4 and 7.5.

The TGA results of PLA in nitrogen (Figure 7.3) show a single mass loss step between 292 – 401^{o}C with mass loss of 99.5% and DTG maximum at 360^{o}C, representing the main decomposition of PLA. This is corroborated by an endothermic DTA peak with maximum at 366^{o}C. The TGA curve of PLA in air shows that PLA decomposes with two mass loss steps. The first step represents the main decomposition of PLA, occurring between 295 – 384^{o}C with the mass loss of 98.6% and DTG maximum at 367^{o}C, the temperature range and DTG max are similar to those observed in nitrogen atmosphere. This decomposition stage is corroborated by a small endothermic DTA peak at 347^{o}C, which is then overlapped with a subsequent large exothermic DTA peak with the peak max at 376^{o}C, similar to that reported by Kandola in another work [4]. The second mass loss step of PLA occurs between 384 - 700^{o}C with 1.4% mass loss, which is accompanied by an exothermic DTA peak at 524^{o}C, representing the oxidation of the char formed in the first step [4,5]. PLA left no char residue at the end of the test.

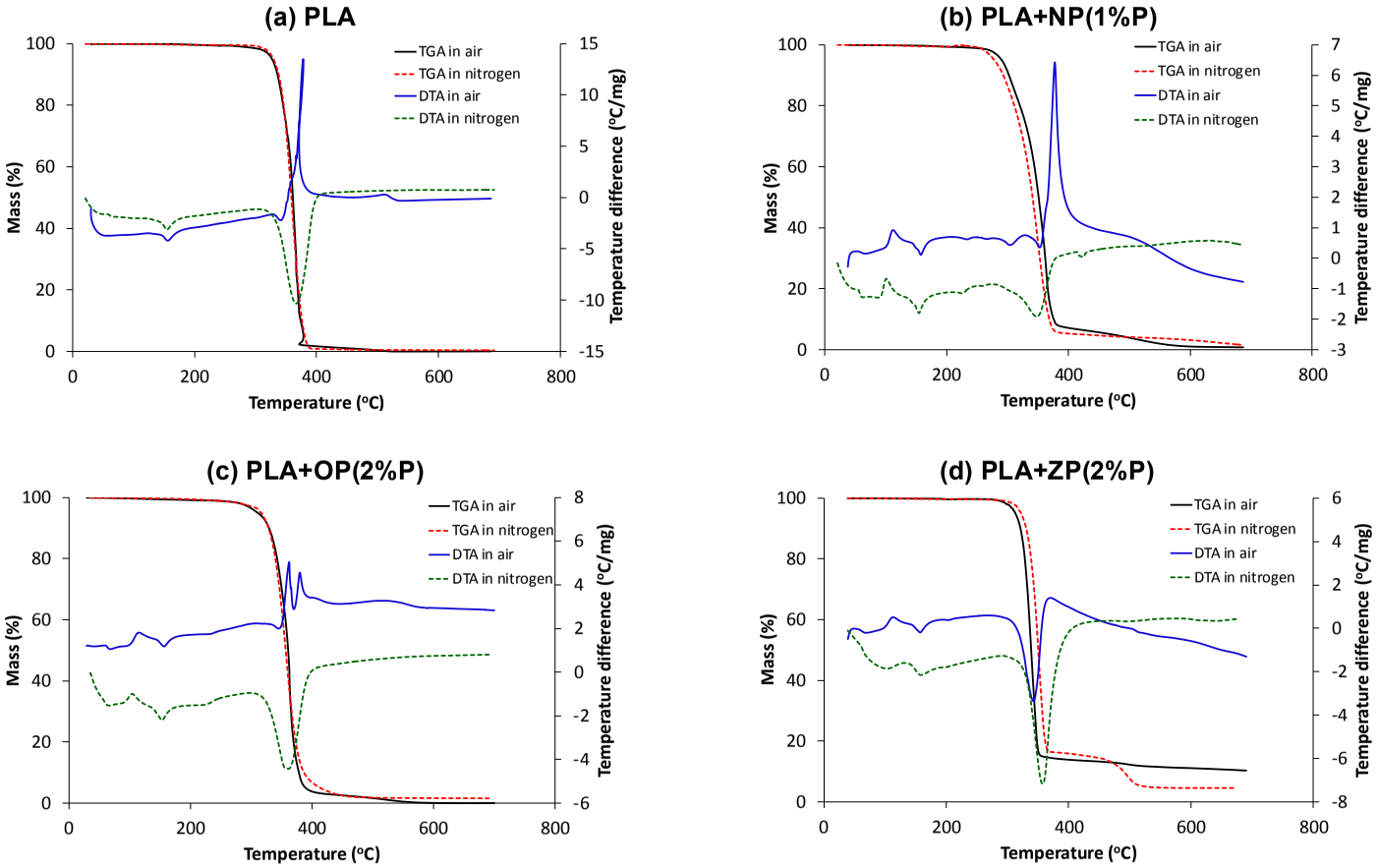

Figure 7.3: TGA and DTA curves of (a) PLA, (b) PLA+NP(1%P), (c) PLA+OP(2%P), and (d) PLA+ZP(2%P) in air and nitrogen

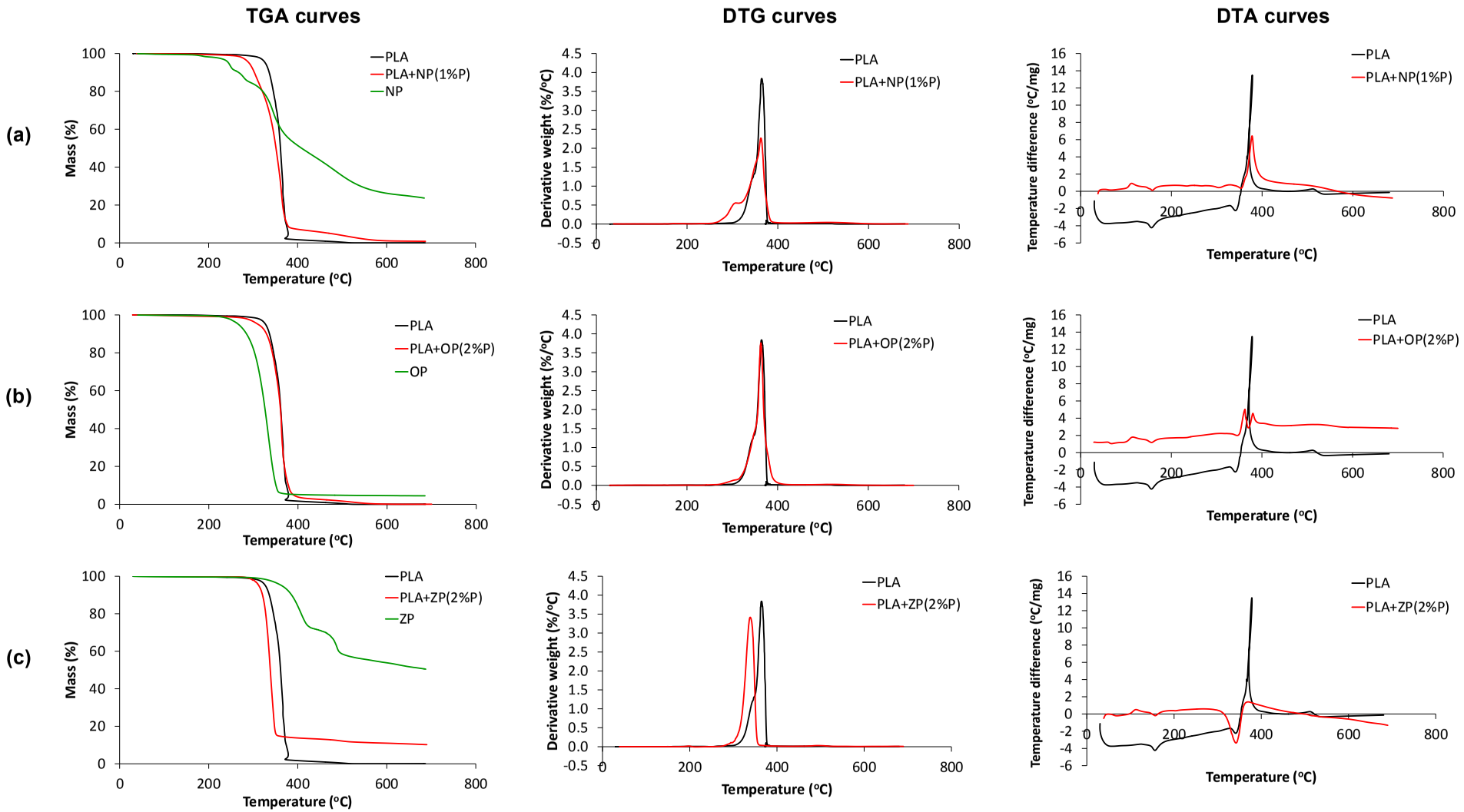

Figure 7.4: TGA, DTG, and DTA curves of PLA containing (a) NP, (b) OP, and (c) ZP flame retardants in air

Table 7.4: TGA, DTG and DTA results of PLA containing NP, OP and ZP flame retardants in nitrogen

Sample	1st mass loss step			2nd mass loss step			Residue at 700°C (%)	DTA peak Max	
	Temp range* (°C)	Mass loss (%)	DTG Max (°C)	Temp range (°C)	Mass loss (%)	DTG Max (°C)		Melting (°C)	Decomposition (°C)
PLA	292* - 401	99.5	360	-	-	-	0.5	155	366 (En)
PLA+NP(1%P)	246*- 388	98.5	350	-	-	-	1.5	154	225,347 (En)
PLA+OP(1%P)	277* - 480	98.4	356	-	-	-	1.6	154	229,361 (En)
PLA+OP(2%P)	280* - 485	98.5	359	-	-	-	1.5	154	232,362 (En)
PLA+ZP(1%P)	274* - 354	88.6	330	354 - 537	5.0	478	6.4	156	195,334 (En)
PLA+ZP(2%P)	285* - 372	83.7	332	372 - 535	11.7	496	4.6	159	197,357 (En)

Note: * = Onset of decomposition temperature; En = endothermic peak; Ex = exothermic peak

Table 7.5: TGA, DTG and DTA results of PLA containing NP, OP and ZP flame retardants in air

Sample	1st mass loss step			2nd mass loss step			Residue at 700°C (%)	DTA peak Max	
	Temp range (°C)	Mass loss (%)	DTG Max (°C)	Temp range (°C)	Mass loss (%)	DTG Max (°C)		Melting (°C)	Decomposition (°C)
PLA	295* – 384	98.6	367	384 – 700	1.4	-	0.0	159	347 (En); 376,524 (Ex)
PLA+NP(1%P)	258* – 392	92.5	303 (s),363	392 – 700	6.7	-	0.8	158	305,353 (En); 378,513 (Ex)
PLA+OP(1%P)	267* – 409	97.3	362	409 – 700	2.5	-	0.2	156	230,342 (En); 370,379,524 (Ex)
PLA+OP(2%P)	268* – 420	96.9	363	420 – 700	2.8	-	0.3	156	233,346 (En); 363,380,522 (Ex)
PLA+ZP(1%P)	265* – 357	91.2	337	357 – 700	2.0	-	6.8	156	203,338 (En); 367,589 (Ex)
PLA+ZP(2%P)	276* – 360	85.3	338	360 – 700	4.5	-	10.2	157	202,342 (En); 370,601 (Ex)

Note: * = Onset of decomposition temperature; En = endothermic peak; Ex = exothermic peak; s = shoulder peak

With the addition of NP flame retardant at 1% P level, the TGA results in nitrogen show that PLA+NP(1%P) decomposes with single mass loss step between 246 – 388°C showing 98.5% mass loss with the DTG max at 350°C, leaving 1.5% residue at 700°C. In air, PLA+NP(1%P) shows two stages of mass loss, representing the main decomposition and char oxidation of the sample, similar to the thermal decomposition of PLA in air. The first stage of PLA+NP(1%P) occurs in the similar temperature range (258 – 392°C) as observed in nitrogen with the DTG max at 303°C (small peak) and 363°C, and mass loss of 92.5%. This is followed by the char oxidation stage between 392 – 700°C, leaving 0.8% residue at the end. These results show that the addition of NP flame retardant causes a reduction in the onset of decomposition temperature of PLA+NP(1%P) in comparison to the control, which could be due to the low thermal stability of NP flame retardant as can be seen in Figure 7.4 (a) that NP flame retardant starts losing weight from 239°C which is much lower temperature than that of the onset of decomposition of PLA. NP flame retardant however reduced the mass loss in the main decomposition stage of PLA from 99.5 to 94.4% in nitrogen and from 98.6 to 92.5% in air, and improved the char formation of PLA from 0% in the control to 0.8% in PLA+NP(1%P). To observe whether there is any interaction between NP flame retardant and PLA polymer, the experimental TGA curve in air of PLA+NP(1%P) is compared with the calculated curve (calculated average from the responses of the individual components with respect to their percent mass fraction as given in Table 7.1) as shown in Figure 7.5.

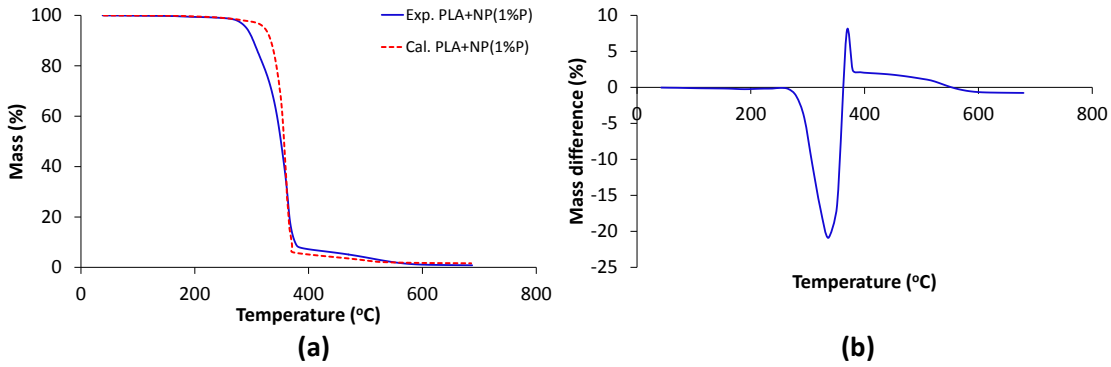

Figure 7.5: (a) Experimental and calculated TGA curves of PLA+NP(1%P) in air, and (b) mass difference curve between the experimental and calculated TGA curves.

In Figure 7.5 (b), the difference between calculated and experimental curves is plotted as a function of temperature. The results show that experimentally PLA+NP(1%P) starts losing mass at lower temperature than expected from the calculated curve, but has better thermal stability in the temperature range between 360 – 550°C (Figure 7.5 (b)). The formed char is however not highly stable as it is oxidised leaving lower residue at 700°C in the experimental curve as compared to the calculated, Figure 7.5 (b). This reveals that there could be a reaction between NP flame retardant and PLA that causes PLA+NP(1%P) to decompose at lower temperature than that of the control PLA, producing slightly more residue in 360 – 550°C. Although the actual chemical composition of NP flame retardant is not known, due to the commercial sensitivity of the product, the interaction can be explained in generic term similar to other P based flame

retardants. On heating, the phosphoric acid is released from the decomposition of the flame retardant, which works as a Lewis acid to react with the polymer through a phosphorylation reaction. As a result of this reaction, the tendency of the polymer to decompose through dehydration reaction is increased, hence producing less flammable products and promoting more char formation [6,7]. This therefore results in the reduction in the flammability of PLA+NP(1%P) in comparison to the control as can be seen from the decrease in the THR, EHC; and the increase in the amount of charred residue in the cone calorimetric results of PLA+NP(1%P) as compared to the control, Table 7.3.

With the addition of OP flame retardant, the TGA results in nitrogen show that PLA+OP(1%P) decomposes with a single mass loss step between 277 – 480^{o}C, showing mass loss of 98.4% and DTG max at 356^{o}C. These results are almost similar to that of the control PLA, except that a small reduction in the onset of decomposition temperature and marginal increase in the char formation in the PLA+OP(1%P) as compared to the control are observed, Table 7.4. On increasing the phosphorus concentration to 2% in sample PLA+OP(2%P), there is not much difference in behaviour as can be seen from Table 7.4. A similar effect is also seen in the TGA results in air where the addition of OP flame retardant did not have significant effect on the thermal decomposition of PLA, as can be seen that the TGA curve of PLA+OP(2%P), which is similar to that of the control Figure 7.4 (b). This indicates a low interaction between OP flame retardant and PLA in the solid phase.

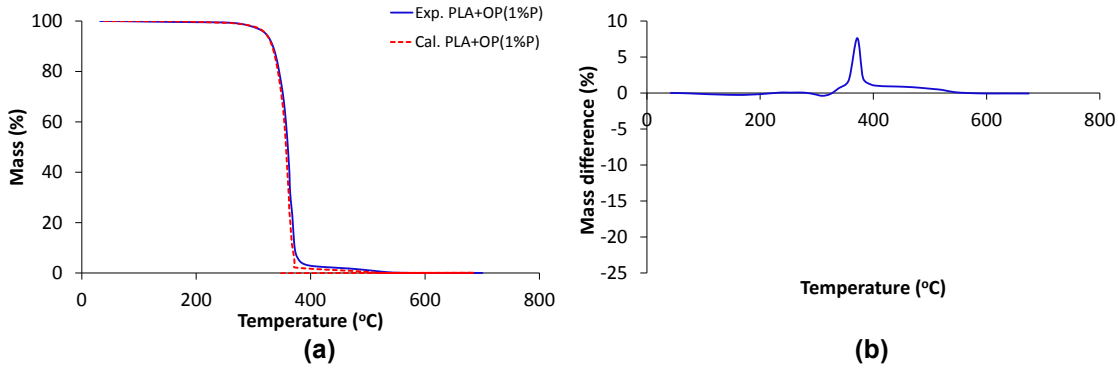

Figure 7.6: (a) Experimental and calculated TGA curves of PLA+OP(1%P) in air, and (b) mass different curve between the experimental and calculated TGA curves

The effect is seen more clearly when comparing the experimental curve of PLA+OP(1%P) with its calculated TGA curve (Figure 7.6), where the experimental curve is similar to the calculated curve with slightly better thermal stability in the temperature range 324 - 550^{o}C (Figure 7.6 (b)). Hence, this suggests that the significant improvement in the fire performance of PLA+OP samples in comparison to the control as observed by LOI, UL-94 and cone tests could be mainly the action in the vapour phase, which is discussed in details later on in this section, although there is a marginal effect of OP flame retardant in the solid phase as well, seen from the TGA results.

In case of ZP flame retardant, the TGA results in nitrogen show that ZP flame retardant causes the PLA to decompose at lower temperature as can be seen from the lower onset of decomposition temperature (274°C) and DTG max (330°C) in PLA+ZP(1%P) as compared to those of the control PLA, Table 7.4. ZP flame retardant however significantly improved the char formation of PLA by increasing the charred residue of PLA from 0.5% in the control to 6.4% in the PLA+ZP(1%P). The same effect is also seen in the TGA results in air atmosphere. The TGA results in air show that PLA+ZP(1%P) decomposes with lower onset of decomposition temperature (265°C) as compared to the control (295°C), and shows the maximum decomposition in the first step at 337°C which is 30°C lower than that of the control. ZP flame retardant increased the charred residue of PLA from 0% in the control to 6.8% in PLA+ZP(1%P). At the higher ZP content, PLA+ZP(2%P) shows similar decomposition behaviour as observed in PLA+ZP(1%P), but higher charred residue (10.2%) is observed, as compared to the PLA+ZP(1%P), Table 7.4.

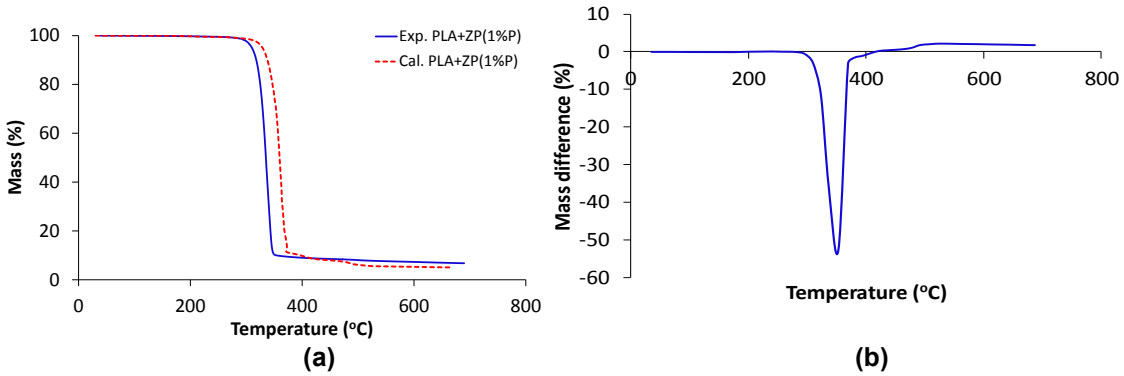

Figure 7.7: (a) Experimental and calculated TGA curves of PLA+ZP(1%P) in air, and (b) mass difference curve between the experimental and calculated TGA curves

On comparing the experimental curve of PLA+ZP(1%P) with its calculated curve, the results show that the experimental curve indicates loss of mass at the lower temperature than the calculated one, Figure 7.7. This is due to ZP flame retardant, which is zinc phosphinate, decomposing on heating to give to zinc oxide and phosphinic acid to react with PLA [8]. The zinc oxide could catalyse the decomposition of PLA through the depolymerisation reaction [9,10], resulting in the decomposition at lower temperature of the PLA+ZP sample. This leads to the reduction in the TTI of PLA+ZP sample in comparison to the control PLA in cone test, Table 7.3. Hence, this leads to the lower FR efficiency of ZP flame retardant compared to other FRs studied here even though ZP flame retardant improved the char formation of PLA (Table 7.5).

To have better understanding on the mechanism of these flame retardants (i.e. vapour or solid phase activity), the gas evolved from thermal decomposition of control and flame retardant PLA samples from room temperature to 700°C in nitrogen were also analysed by using TGA coupled with FTIR (TG-IR) as this gives an indication of the products of decomposition in the gas phase without the effect from oxidation caused by oxygen in the air. The IR spectra of the evolved gases at different temperatures of control and flame retardant PLA samples are presented in Figure 7.8.

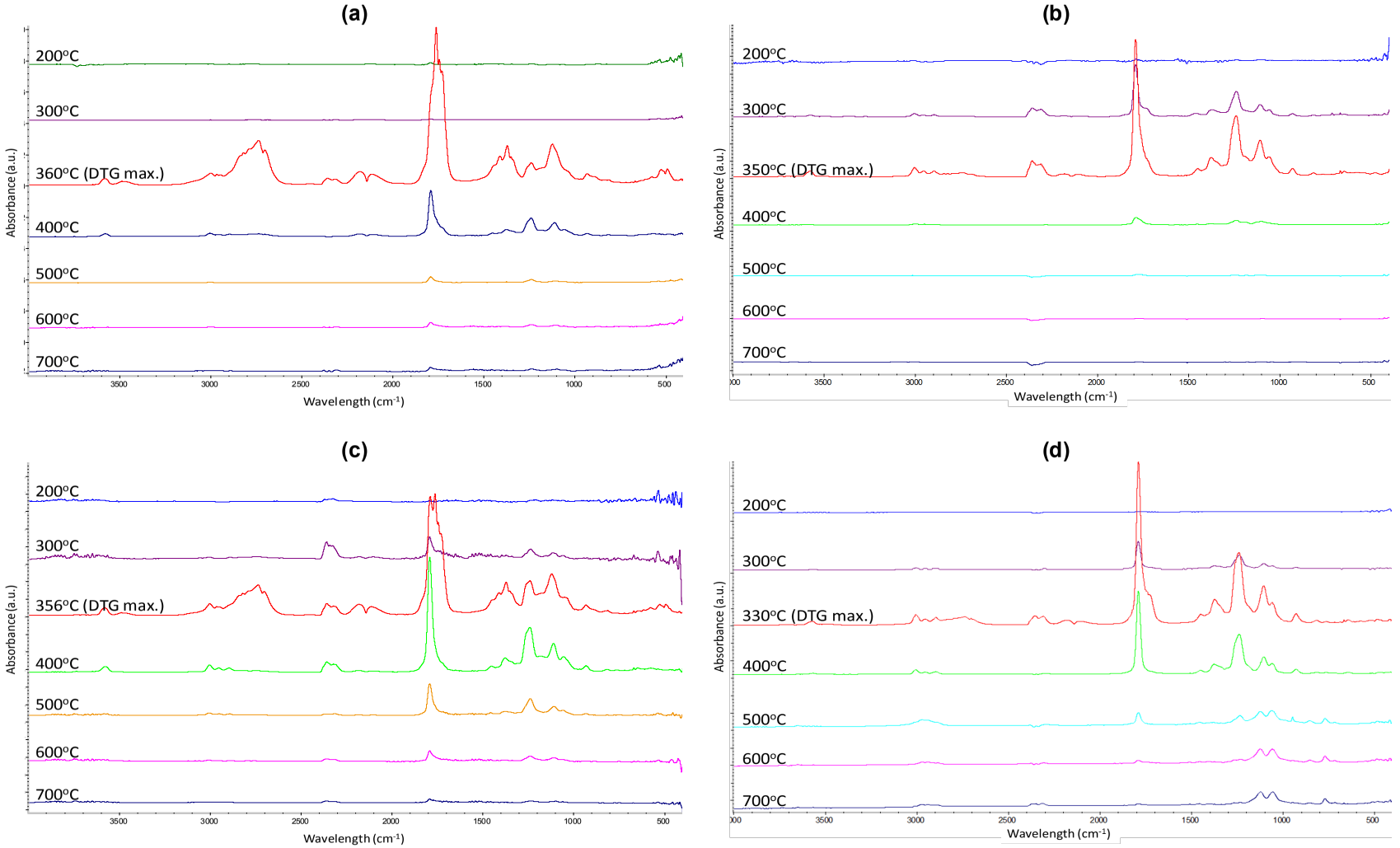

Figure 7.8: IR spectra of evolved gases from the decomposition of (a) PLA, (b) PLA+NP(1%P), (c) PLA+OP(1%P), and (d) PLA+ZP(1%P) in nitrogen at different temperatures

As can be seen from Figure 7.8, the maximum intensity of IR absorbance peaks of the volatiles from the decomposition of control and flame retardant PLA in nitrogen are observed at their DTG max in all samples. In Figure 7.9 (a), the IR spectrum of the gas evolved at 360^{o}C (DTG max) from decomposition of PLA shows the important peaks to be at 2980 – 2740 cm^{-1} (C-H stretching); 2360 and 2320 cm^{-1} (O=C=O stretching); 2180 and 2110 cm^{-1} (C≡O); 1760 cm^{-1} (C=O stretching); and 1260 cm^{1} (C-O stretching) [11,12]. These indicate that on heating PLA releases volatiles such as aliphatic hydrocarbon (2980-2740 cm^{-1}), carbon dioxide (CO_2, 2360 and 2320 cm^{-1}), carbon monoxide (CO, 2180 and 2110 cm^{-1}), and aliphatic carboxylic acid (1760, 1260 cm^{-1}) [13,14].

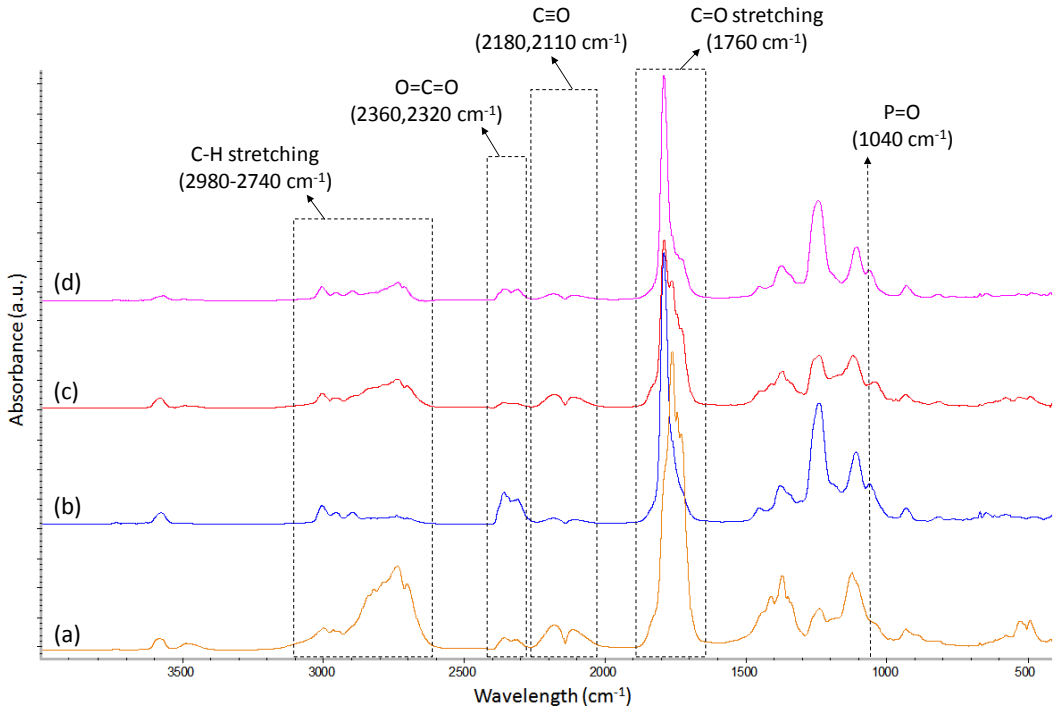

Figure 7.9: IR spectra of the volatiles from the decomposition of (a) PLA, (b) PLA+NP(1%P), (c) PLA+OP(1%P), and (d) PLA+ZP(1%P) in nitrogen at their respective DTG max temperature

With the addition of NP flame retardant, the IR spectra in Figure 7.9 show that the presence of NP flame retardant causes a disappearance of the aliphatic hydrocarbon IR peaks (2980 - 2740 cm^{-1}), and the presence of a peak at 1040 cm^{-1} (P=O stretching) in the spectrum of PLA+NP(1%P) as compared to the control. The disappearance of the aliphatic hydrocarbon peaks could be due to the FR activity of NP flame retardant in condensed phase of PLA that improves char formation of the PLA at the expense of flammable volatiles as discussed above, hence resulting in the significant reduction in the amount of aliphatic hydrocarbon, which is a flammable gas, in the vapour phase of PLA+NP(1%P) as compared to the control. The appearance of IR peaks at 1040 cm^{-1} (P=O stretching) could be explained that on heating NP flame retardant releases PO radicals in the gas phase, which can then subsequently work as a free radical scavenger to interfere with the combustion of the polymer [7]. Due to the reduction in the hydrocarbon flammable gas and the production of the free radical scavenger species in the gas phase, there is a significant improvement in the reduction in flammability of

PLA+NP(1%P) in comparison to the control PLA as discussed in *Section 7.1.1.1*. In the case of PLA+OP(1%P) the IR spectra in Figures 7.9 (a) and (c) show that the IR spectrum of the PLA+OP(1%P) is similar to that observed for the control PLA, except for the appearance of the peak at 1040 cm^{-1} (P=O stretching). This indicates that on heating OP flame retardant releases PO radicals to interfere with the combustion of the polymer [7]. This therefore results in the reduction in the flammability of PLA+OP samples as compared to the control (Table 7.3). With ZP flame retardant, Figure 7.9 (d) shows that the IR spectrum of PLA+ZP(1%P) is similar to that observed for PLA+NP(1%P), as in comparison to the spectrum of PLA the presence of ZP flame retardant causes a reduction in the intensity of the aliphatic hydrocarbon IR peaks (2980 – 2740 cm^{-1}), and the appearance of P=O containing species (1040 cm^{-1}) in the spectrum of PLA+ZP(1%P). This therefore leads to the reduction in flammability of PLA+ZP(1%P) in comparison to the control, as fewer flammable volatiles (i.e. aliphatic hydrocarbon gas) are produced, and the presence of PO radicals in the gas phase could help to inhibit the combustion of the sample.

7.1.1.3 Fibre extrusion of flame retardant PLA

Since the main aim was to develop FR formulations for producing FR-PLA fibres to be used as part of flax/PLA commingled fabrics, the fibre extrusion processability of these FR-PLA samples was also investigated. To explore the fibre extrusion processability of the FR-PLA samples, the standard extruding condition was firstly established by using the control PLA in order for this to be used as a guiding condition to start with the FR-PLA samples. Prior to the fibre extrusion, pellets of control PLA were dried at 50^{o}C for 12 h in order to remove the moisture in the sample as this could cause a partial degradation of PLA during processing at high temperature. PLA is usually processed at a temperature of 200^{o}C. Since OP and ZP flame retardants are melt-blendable at 230^{o}C and 200^{o}C, respectively (also seen from the DTA results in Table 7.5), to ensure that these FRs can melt during fibre extrusion the higher temperature of 230^{o}C was used for processing PLA in this case. The dried PLA pellets were fed into a FET melt-spinning fibre extrusion machine (see *Section 3.2.3*) setting the maximum processing temperature at 230^{o}C using the temperature profile from the feeding hopper to the spinneret die head as given in Table 7.6 in order to melt the PLA polymer. The molten PLA was conveyed to the spinneret head to extrude into filaments through a 20 holes (800 µm diameter) spinneret die. The extruded filaments were cooled down by using an air quench operating at 15^{o}C. The filaments were subsequently drawn by using three sets of heated godets setting the temperature at 65, 70, and 70^{o}C, respectively. The maximum drawing ratio that could be achieved without breaking the filaments was 1:1.2, obtained by setting the rotating speed of the three sets of heated godets at 100, 110 and 120 m/min, respectively. The PLA filaments so produced have 52.5 µm diameter, and 26.3 dTex (g/10,000 m) linear density.

Table 7.6: Fibre extrusion processing parameters and the physical properties of FR-PLA filaments

Sample	Processing temperature (°C)	Temperature profile of the extruder (°C)	Godets temperature (°C)	Godets speed (m/min)	Filaments	
					Diameter (µm)	Linear density (dTex)
PLA	230	190/200/210/220/230/220/200	65/70/70	100/110/120	52.5 ±2.4	26.3 ±0.9
PLA+NP(1%P)*	230	190/200/210/220/230/220/210	-	-	-	-
	200	190/190/190/190/200/200/190	-	-	-	-
PLA+OP(1%P)	230	190/200/210/220/230/220/200	65/70/70	200/240/260	40.1 ±1.2	18.9 ±3.3
PLA+OP(2%P)					42.1 ±2.2	19.7 ±2.1
PLA+ZP(1%P)	230	190/200/210/220/230/220/200	65/70/70	100/105/110	60.4 ±3.2	33.1 ±2.3
PLA+ZP(2%P)					63.1 ±3.8	35.9 ±3.2

* Filaments could not be produced due to the viscosity of the molten polymer was too low to process

These extruding parameters for the control PLA were then used as a guiding condition for the FR-PLA samples. For the PLA+NP(1%P), on using the standard conditions explained above the molten polymer coming off the spinneret die had a very low viscosity, and kept dropping from the spinneret die. This results in unstable flow of the molten PLA+NP(1%P), and hence filaments could not be produced. The second trial on the PLA+NP(1%P) was therefore attempted at lower temperature than the standard condition, expected to reduce the degree of melting in order to achieve the higher viscosity of the molten polymer. The processing temperature in the second attempt was reduced to 200^{o}C (Table 7.6). The results showed that the viscosity of molten PLA+NP(1%P) was also too low to be processable. These results reveal the poor fibre extrusion processability of NP flame retardant in PLA polymer, and hence it can be concluded that NP flame retardant is not suitable for the production of FR-PLA fibres.

On the other hand, the fibre extrusion of PLA+OP(1%P) at 230^{o}C using the standard temperature profile (Table 7.6) showed a stable flow of molten polymer coming off the spinneret. The viscosity of the molten PLA+OP(1%P) was however slightly low, providing a high flow rate in comparison to the control PLA. Hence, in order to have enough tension on the extruded filament to obtain a stable process, the rotating speed of three sets of heated godets were set at higher speed than the standard condition at 200 m/min in the first set of the godets, followed by 240 m/min and 260 m/min in the second and third set, respectively. This therefore results in the drawing ratio of 1:1.3 in PLA+OP(1%P) filaments, and thinner filaments of PLA+OP(1%P) as compared to the control with the diameter of 40.1 μm and 18.9 dTex linear density. At higher OP content, the filaments of PLA+OP(2%P) could also be produced by using the same condition as in PLA+OP(1%P) sample. The diameter and linear density of PLA+OP(2%P) filaments were 42.1 μm and 19.7 dTex, respectively. For ZP flame retardant, PLA+ZP(1%P) with the use of standard extrusion temperature (230^{o}C) was melted, and produced stable filaments coming off the spinneret. The filaments of PLA+ZP(1%P) were however more brittle than the control PLA, hence the filaments could not be drawn at the same ratio (1:1.2 drawing ratio) as the standard condition as used for PLA due to the filaments repeatedly breaking. The rotating speed of the heated godets were therefore changed to provide a lower drawing ratio of 1:1.1 in order to obtain the stable drawing process without causing breakage of the filaments, Table 7.6. This results in the larger diameter (60.4 μm) and higher linear density (33.1 dTex) of PLA+ZP(1%P) filaments, as compared to the control PLA. By using the same processing condition as PLA+ZP(1%P), PLA+ZP(2%P) filaments could also be produced having 63.1 μm diameter and 35.9 dTex linear density. From these fibre extrusion results, it can be concluded that in terms of fibre extrusion processability, OP and ZP flame retardants were suitable for producing the FR-PLA fibres, whereas NP flame retardant was not. These were as expected as OP and ZP flame retardants are melt-blendable flame retardants, hence providing better fibre extrusion processability as compared to NP flame retardant.

7.1.2 Flame retardant polypropylene (FR-PP) polymers/fibres

From the outcome of the study of FR-PLA fibres above, OP flame retardant which showed relatively high FR performance and good fibre extrusion processability was chosen for developing FR-PP fibres in this section. The FR-PP samples were prepared by compounding PP with OP flame retardant at 1 and 2% P levels by using a twin-screw extruder. The compounded FR-PP samples were then melt-pressed to 3 mm plaques for flammability testing.

7.1.2.1 Flammability of flame retardant PP

The flammability of the control and FR-PP plaques tested by LOI and UL-94 are reported in Table 7.7. The results show that PP has an LOI value of 18.0%. On addition of OP flame retardant, the LOI of PP was increased to 20.6 and 21.4% with 1 and 2% P content of OP flame retardant, respectively.

Table 7.7: LOI and UL-94 results of PP containing OP flame retardant

Sample	LOI	UL-94 horizontal	UL-94 vertical	
	(%)	B. Rate (mm/min)	B. Rate (mm/min)	V-Rate
PP	18.0	36.7 ±5.2	77.6 ±3.2	Failed
PP+OP(1%P)	20.6	-*	-*	V-2
PP+OP(2%P)	21.4	-*	-*	V-2

* The flame went out with melt-dripping soon after removal of the flame

The UL-94 vertical test results were as expected. Due to the low LOI of PP, it failed to rank in the vertical rating classification as the sample burned up to the sample holder with the rate of burning being 77.6 mm/min. With the presence of OP flame retardant at 1% P level, the fire performance of PP was improved from no rating to V-2 rating. Although the sample did not burn, the V-2 rating arose from the flaming drops of the specimen causing ignition of the cotton underneath. At 2% P content of OP flame retardant, PP+OP(2%P) also show the same rating (V-2) as observed for PP+OP(1%P) as flaming drips also caused ignition of the cotton. The UL-94 horizontal test results show that the control PP burned with a 36.7 mm/min rate of burning. On addition of OP flame retardant, the horizontal rate of burning of the samples could not be measured since with both 1 and 2% P the flame went out the specimen with the flaming drips before reaching the timing mark.

The fire performance of these samples of PP containing OP flame retardant was also evaluated compared to the control PP by using cone calorimetry at 35 kW/m^2 heat flux. The HRR, RSR, and mass loss curves of these samples are presented in Figure 7.10, and the derived results from the curves are reported in Table 7.8.

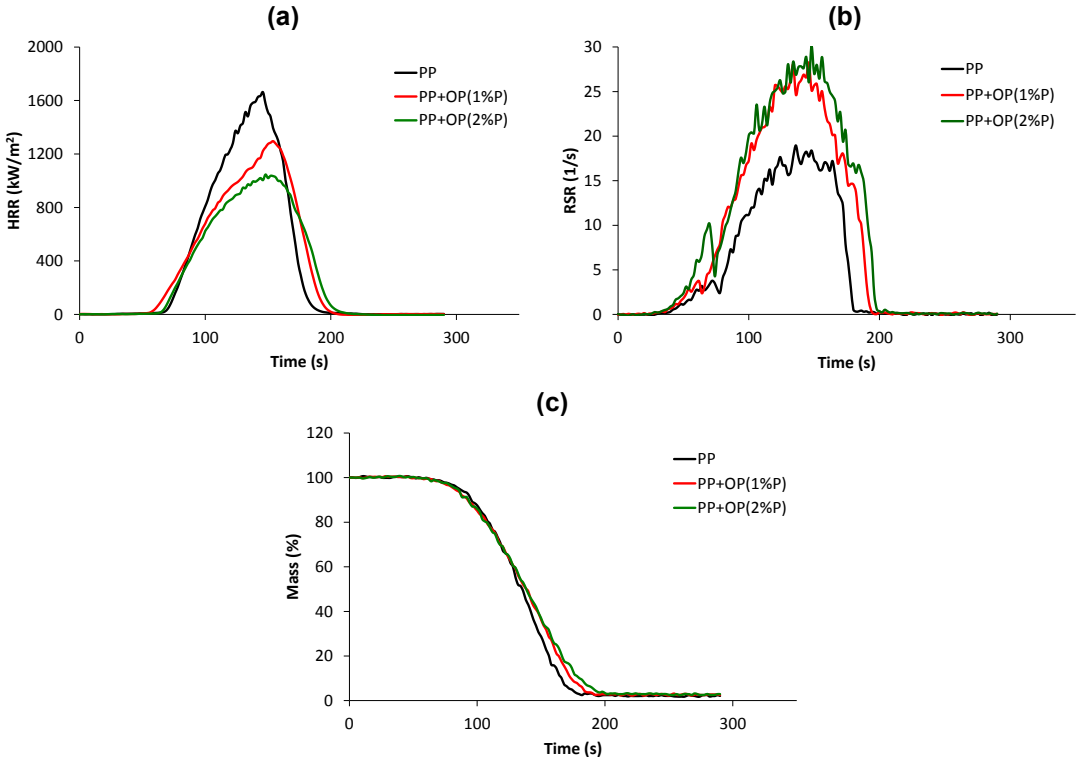

Figure 7.10: The cone calorimetric results of PP containing OP flame retardant plaques at 35 kW/m^2: (a) HRR, (b) RSR, and (c) mass loss curves as a function of time

Table 7.8: Cone calorimetric results of PP containing OP flame retardant at 35 kW/m^2

Sample	TTI (s)	t_{PHRR} (s)	PHRR (kW/m^2)	THR (MJ/m^2)	EHC (MJ/kg)	TSR (L)	Yield (%)	Fire rating parameters	
								FPI (s/(kW/m^2))	FIGRA ((kW/m^2·s)
PP	74 ±1	144 ±3	1632 ±43	106 ±1	44 ±1	1387 ±97	0.0 ±3.3	0.05 ±0.01	11.3 ±0.1
PP+OP(1%P)	64 ±4	155 ±3	1307 ±103	98 ±2	39 ±1	2284 ±107	2.5 ±0.6	0.05 ±0.01	8.8 ±0.3
PP+OP(2%P)	71 ±1	148 ±1	1047 ±26	88 ±4	36 ±1	2524 ±168	2.9 ±0.4	0.07 ±0.01	7.1 ±0.2

As can be seen from Table 7.8, PP ignited at 74 s, and burned with a high PHRR of 1632 kW/m^2 producing 106 MJ/m^2 of THR. PP released 1387 L of TSR, and produced no charred residue. With the presence of OP flame retardant in sample PP+OP(1%P), the results show lower TTI of 64 s than the control at 74 s, but burned with the lower PHRR (1307 kW/m^2) and THR (98 MJ/m^2) in comparison to the control. PP+OP(1%P) released very high volume of smoke (2284 L TSR), and produced some charred residue (2.5%), Table 7.8. At 2% P content of OP flame retardant, the FR performance of OP flame retardant was further enhanced as can be seen that PP+OP(2%P) ignited at 71 s, and burned with the lower PHRR (1047 kW/m^2) as compared to that PP+OP(1%P), and produced the lower THR of 88 MJ/m^2, but similar char. On comparing the fire performance index (FPI) of the control and PP+OP samples in Table 7.8, the results show that the addition of OP flame retardant at 2% P content slightly improved the fire performance of PLA as it increased the FPI of PLA from 0.05 s/(kW/m^2) in the control to

0.07 s/(kW/m^2), whereas at lower OP content (1%P) no improvement was observed. These cone calorimetric results indicate that the flammability of PP was reduced with the presence of OP flame retardant. However, the FR efficiency of OP flame retardant in PP was less than in PLA polymer, as in PP polymer, OP flame retardant only reduced the PHRR without improving other parameters, i.e. TTI and char formation, which might also have helped in improving the overall fire performance of the sample. Moreover, the OP flame retardant although reducing the PHRR of PP, the PHRR values were still relatively high, particularly compared to that of the PLA+OP samples, hence a smaller improvement in the fire retardancy of PP+OP samples was observed (i.e. V-2 rating achievement) in comparison to the PLA+OP (i.e. V-0 rating achievement). The FIGRA results also show a similar trend to that in FPI, as the results show that the addition of OP flame retardant decreased the FIGRA of PP from 11.3 kW/m^2·s in the control to 8.8 and 7.1 kW/m^2·s with 1 and 2% P OP content, indicating the improvement in fire safety rating of PP+OP samples as compared to the control.

7.1.2.2 Thermal decomposition of flame retardant PP

The thermal analysis of PP+OP samples was conducted by using thermogravimetric analysis (TGA) in air and nitrogen atmosphere from room temperature up to 700^{o}C in order to understand the action of OP flame retardant on the reduction in flammability of PP+OP samples as compared to the control PP. The TGA in nitrogen and air of PP, PP+OP(1%P) and PP+OP(2%P) are shown in Figure 7.11 and analysed results are reported in Table 7.9 and 7.10, respectively. The TGA results in nitrogen show that PP decomposes with a single mass loss step between 377 – 483^{o}C, showing mass loss of 99.7% and DTG max at 454^{o}C. In air, PP shows one large decomposition stage in the temperature range between 238 – 380^{o}C with the mass loss of 97.3%, which is corroborated by a large exothermic DTA peak at 365^{o}C representing the main decomposition of PP. This is followed by the small mass loss step between 380 – 700^{o}C, accompanied by the small exothermic DTA peak at 465^{o}C, representing the oxidation of the products formed in the first step. The TGA results in air also show that PP produced almost no char residue (0.1%) which is as expected since PP contains only hydrogen and carbon in its polymeric structure, and decomposes with low char formation [15-17]. These results show that the thermal stability of PP in air is much lower than in nitrogen as it decomposes at much lower temperature in air (238 – 380^{o}C) as compared to that in nitrogen (377 – 483^{o}C) which is because oxygen in the air causes auto-oxidation of PP during the decomposition [17].

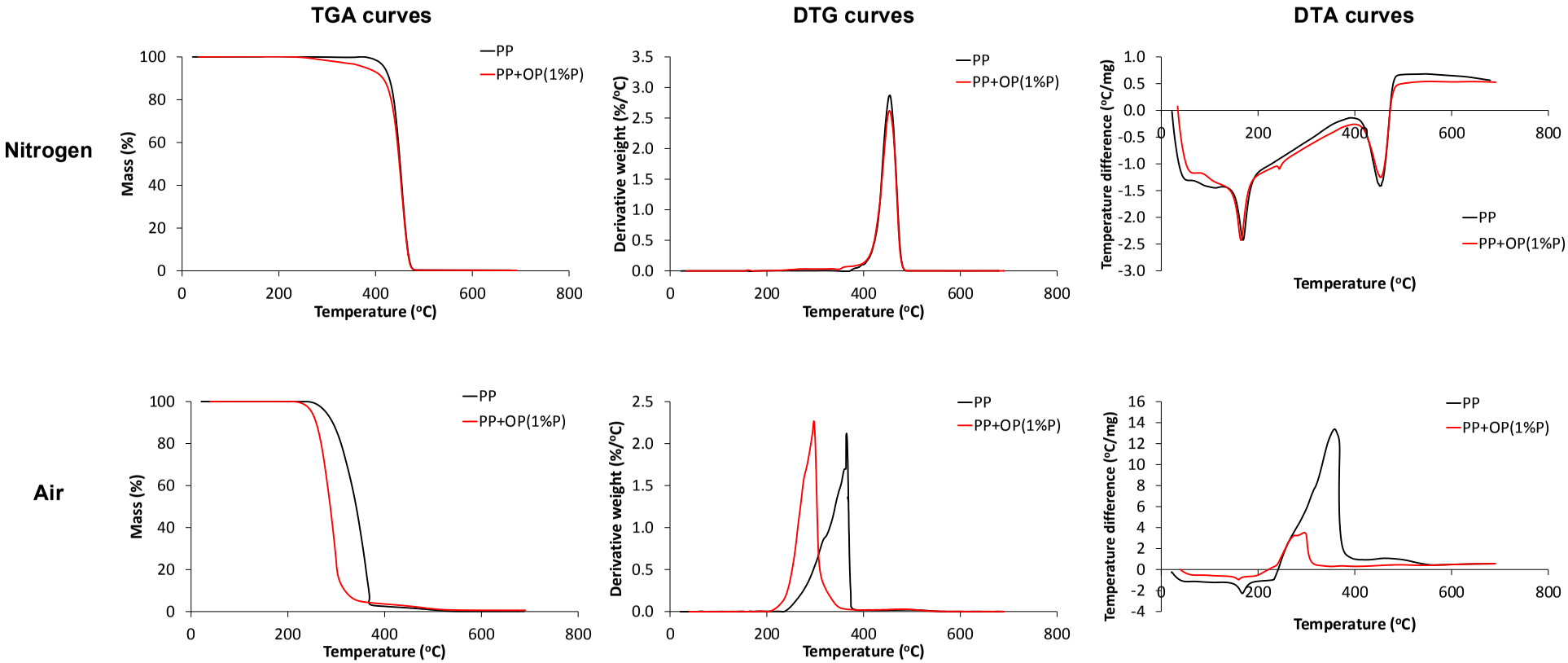

Figure 7.11: TGA, DTG, and DTA curves of control PP and PP+OP(1%P) in nitrogen and air

Table 7.9: TGA, DTG and DTA results of PP containing OP flame retardant in nitrogen

Sample	1st mass loss step			Residue at 700°C (%)	DTA peak Max	
	Temp range (°C)	Mass loss (%)	DTG Max (°C)		Melting (°C)	Decomposition (°C)
PP	377* – 483	99.7	454	0.3	169 (En)	452 (En)
PP+OP(1%P)	250* – 491	99.7	453	0.3	165 (En)	244,454 (En)
PP+OP(2%P)	250* – 490	99.5	454	0.5	166 (En)	245,455 (En)

Note: * = Onset of decomposition temperature; En = endothermic peak; Ex = exothermic peak

Table 7.10: TGA, DTG and DTA results of PP containing OP flame retardant in air

Sample	1st mass loss step			2nd mass loss step			Residue at 700°C (%)	DTA peak Max	
	Temp range (°C)	Mass loss (%)	DTG Max (°C)	Temp range (°C)	Mass loss (%)	DTG Max (°C)		Melting (°C)	Decomposition (°C)
PP	238* - 380	97.3	365	380 – 700	2.6	-	0.1	168 (En)	358,465 (Ex)
PP+OP(1%P)	209* - 362	95.6	297	362 – 700	3.8	-	0.6	160 (En)	240 (En); 296,492 (Ex)
PP+OP(2%P)	214* - 356	94.3	295	356 – 700	5.0	-	0.7	160 (En)	241 (En); 287,486 (Ex)

Note: * = Onset of decomposition temperature; En = endothermic peak; Ex = exothermic peak

On addition of OP flame retardant, the TGA results in nitrogen of PP+OP(1%P) show that OP flame retardant reduced the onset of decomposition temperature of PP, but did not extensively change the decomposition as can be seen that PP+OP(1%P) although starting to lose mass at lower temperature (250^{o}C) than the control (377^{o}C), then decomposes with similar behaviour as in PP in the temperature range of 430 – 700^{o}C, Figure 7.11. In air, PP+OP(1%P) decomposes with one large mass loss step between 209 – 362^{o}C with a DTG peak at 297^{o}C, showing 95.6% mass loss. And, between 362 – 700^{o}C the decomposed product formed in the first step is oxidised, leaving 0.6% charred residue at the end. At higher FR content, the TGA results show no clear effect from the increased OP content as seen by the similar TGA curves of PP+OP at 1 and 2% P. These results demonstrate that OP flame retardant causes a reduction in the thermal stability of PP, particularly in air atmosphere, to decompose with higher mass loss in the lower temperature range. In comparison between the experimental and the calculated TGA curves in air of PP+OP samples (Figure 7.12), the results show that in the experimental curve, mass loss starts at a lower temperature than in the calculated one.

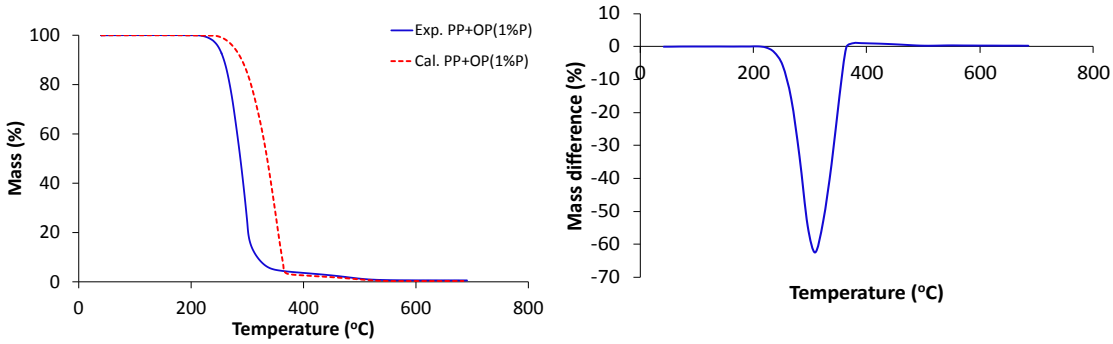

Figure 7.12: (a) Experimental and calculated TGA curves of PP+OP(1%P) in air, and (b) mass difference curve between the experimental and calculated TGA curves

In fact, the decrease in thermal stability of PP+OP samples was not expected as the flammability results in *Section 7.1.2.1* show that the fire retardancy of PP was improved with the presence of OP flame retardant. This therefore suggests that the improvement in the fire retardancy of PP+OP, as compared to the control PP, would be due to the vapour phase activity of OP flame retardant similar to that observed in PLA+OP samples. To support this hypothesis, the evolved gases collected from the thermal decomposition of PP and PP+OP(1%P) in nitrogen atmosphere from room temperature to 700^{o}C were analysed. The IR spectra of the gases released from thermal decomposition of PP and PP+OP(1%P) at different temperatures are given in Figure 7.13 and 7.14, respectively.

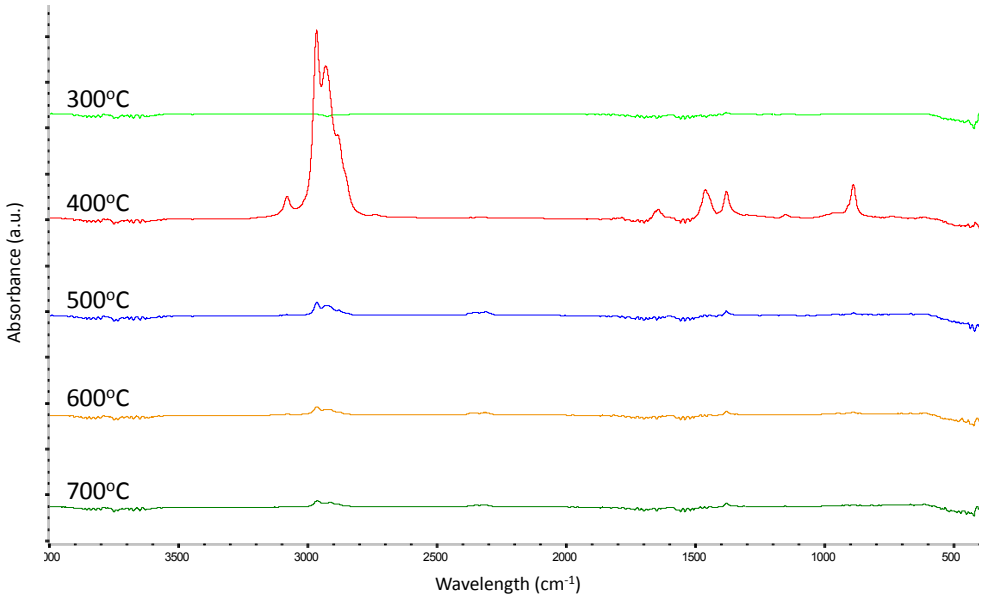

Figure 7.13: IR absorbance spectra of gases released from the thermal decomposition of PP in nitrogen atmosphere at different temperatures

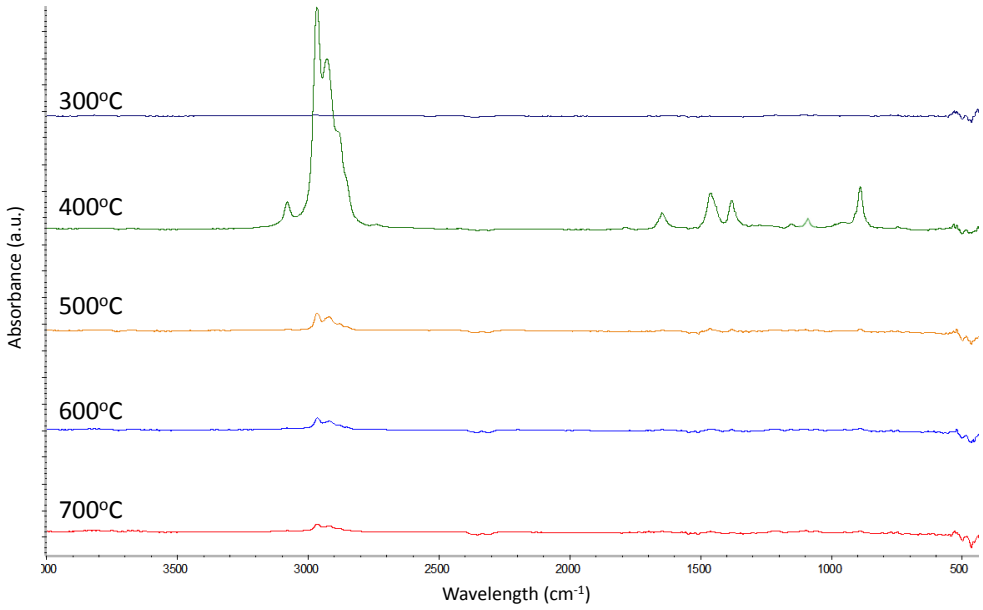

Figure 7.14: IR absorbance spectra of gases released from the thermal decomposition of PP+OP(1%P) in nitrogen atmosphere at different temperatures

The IR peaks of the evolved gaseous from the decomposition of PP are mainly observed at 400°C (Figure 7.13), and show the peaks at 3080 cm^{-1} (C=CH stretching); 2965 and 2930 cm^{-1} ($-CH_3$ stretching); 1650 cm^{-1} (C=C stretching); 1460 cm^{-1} ($-CH_2-$ vibration); 1380 cm^{-1} ($-CH_3$ bending); and 890 cm^{-1} ($C=CH_2$ deformation) [11,12]. This indicates that on decomposition of PP, alkanes (IR peaks: 2965, 2930 cm^{-1}), alkenes (IR peaks: 3080, 1650 cm^{-1}), and dienes (IR peaks: 1460, 890 cm^{-1}) are produced [16,18]. With the addition of OP flame retardant, the results show that the gases released from the decomposition of PP+OP(1%P) show similar peaks as in the PP, but there is an additional small peak at 1040 cm^{-1} (P=O stretching) corresponding to the PO radicals produced from the decomposition of OP flame retardant,

Figure 7.15. From these results, the FR activity of OP flame retardant on PP polymer therefore could be explained by the free radical quenching effect in the gas phase of the samples as the PO free radicals produced from OP flame retardant could inhibit the combustion of PP, hence resulting in the reduction in the flammability of PP+OP samples in comparison to the control (Table 7.8).

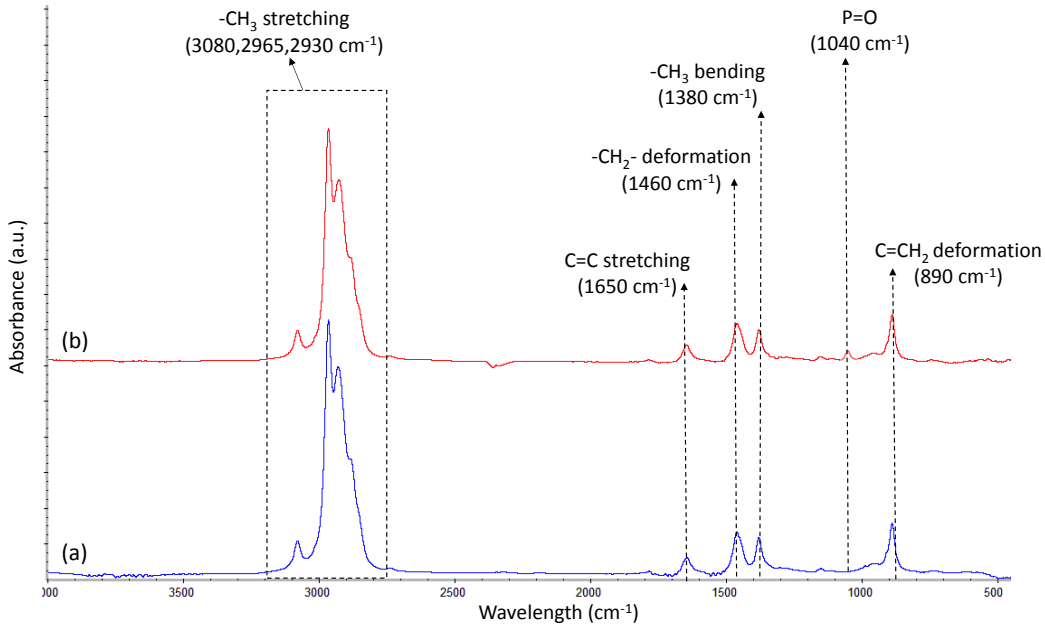

Figure 7.15: IR spectra of the volatiles evolved from the decomposition of (a) PP and (b) PP+OP(1%P) in nitrogen at 400°C

7.1.2.3 Fibre extrusion of flame retardant PP

The fibre extrusion processabilities of these PP containing OP flame retardant samples were investigated to identify its suitability for producing FR-PP fibres to be used in a commingled flax/PP fabric. The standard processing condition was firstly established by using the control PP. Due to the similar melting temperature between PP and PLA polymers, the processing temperature of PP fibres was also chosen at 230°C (i.e. same as used in PLA samples in *Section 7.1.1.3*). The control PP was extruded into filaments by using the FET melt-spinning fibre extrusion machine at 230°C, the setting of temperature profile of the barrel of the extruder is given in Table 7.11. The extruded PP filament coming off the spinneret die were cooled down by using an air quench operating at 15°C, and then subsequently drawn by using three sets of heated godets setting the temperature at 25, 40, and 50°C, respectively. The maximum drawing ratio without causing the breakage of PP filaments could be achieved at 1:4 by setting the rotating speed of the godets at 100 m/min in the first set of godets, 200 m/min in the second, and 400 m/min in the third. The produced PP filaments have 37.2 µm diameter and 9.4 dTex linear density.

Table 7.11: Fibre extrusion processing parameters and the physical properties of FR-PP filaments

Sample	Processing temperature (°C)	Temperature profile of the extruder (°C)	Godets temperature (°C)	Godets speed (m/min)	Filaments	
					Diameter (µm)	Linear density (dTex)
PP	230	185/200/215/230/230/230/230	25/40/50	100/200/400	37.2 ±1.5	9.4 ±1.1
PP+OP(1%P)	230*	185/200/215/230/230/230/230	-	-	-	-
	250	185/200/215/230/250/250/250	25/40/50	100/120/150	49.5 ±2.4	18.3 ±3.9
PP+OP(2%P)	250*	185/200/215/230/250/250/250	-	-	-	-

* Filaments could not be produced

On using the standard parameters, established by using the control PP as discussed above, to extrude PP+OP(1%P) filaments, the results showed that the extruded PP+OP(1%P) filaments have rough surfaces, causing the breakage of the filaments when drawing the filaments from the spinneret die to the first set of godets. This suggested the incomplete melting of the OP flame retardant, as when referred to the DTA results in Table 7.10 it can be seen that the melting temperature of OP flame retardant in PP+OP samples (i.e. ~240^{o}C) is slightly higher than that observed in PLA samples (i.e. 230^{o}C). Hence, to ensure that OP flame retardant can melt at processing temperature of PP+OP samples, the second fibre extrusion trial was attempted at 250^{o}C. The results at 250^{o}C showed that the extruded filaments had smoother surfaces, and provided a stable drawing process. However, the PP+OP(1%P) filaments were more brittle than the control PP, and hence the filaments could not be drawn at the same ratio (1:4) as used in the PP filaments due to the fact that PP+OP(1%P) filaments kept breaking. Therefore to keep the running process stable, the speeds of the second and the third set of the godets were reduced to 120 m/min and 250 m/min, respectively. This results in the lower drawing ratio of 1:1.5 on the PP+OP(1%P) filaments, and thicker filaments in comparison to the control PP. The diameter and linear density of PP+OP(1%P) are 49.5 μm and 18.3 dTex, respectively. For the PP+OP(2%P), by using the same conditions as for the successfully extruded PP+OP(1%P) at 250^{o}C, the results showed that the molten polymer of PP+OP(2%P) could be extruded through the spinneret die of the extruder, but the filaments were very brittle, and could not be handled, as the filaments kept breaking even when collected by hand without going through the drawing process. This therefore leads to the conclusion that the maximum OP flame retardant content in PP that is suitable to process to filaments was limited to 1% P level (8.4% solid content).

7.2 Flame retardant poly(furfuryl alcohol) (FR-Furan)

Although furan resin is not very flammable in nature, when used with natural fibres to produce composites, the high flammability of the natural fibres could cause a reduction in the fire performance of the derived composites. Hence the development of flame retardant furan resin has also been attempted here to reduce the overall flammability of composites. To render polyfurfuryl alcohol (furan resin) flame retardant, a number of different P based flame retardants (FRs) were used. The flame retardants selected here were from those widely used for thermoset resins, namely RDP (resorcinol bis(diphenyl phosphate)), BAPP (bisphenol A bis(diphenyl phosphate)), DOPO (9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide), APP (ammonium polyphosphate) and MPP (melamine polyphosphate). Plaques of furan resin containing these FRs to obtain specific P contents were prepared by mixing FRs with liquid resin, and then casting into 3 mm plaques by using the procedure explained in *Section 3.2.1.2 (Chapter 3)*. The details of the prepared FR-Furan samples are given in Table 7.12.

Table 7.12: Details of furan resin containing different P based flame retardants

Sample	P content (%)	N content (%)
Furan	-	-
Furan + RDP (1.1%P)	1.1	-
Furan + BAPP (0.9%P)	0.9	-
Furan + DOPO (1.6%P)	1.6	-
Furan + DOPO (3.2%P)	3.2	-
Furan + MPP (1.3%P)	1.3	4.2
Furan + MPP (2.6%P)	2.6	8.4
Furan + APP (3.0%P)	3.0	1.4
Furan + APP (6.0%P)	6.0	2.8

Note: Due to high viscosity of the mixture during sample preparation, the samples containing RDP and BAPP at higher FR content could not be prepared.

The cross section of the control and flame retardant furan plaque samples were examined by optical microscopy to see the dispersion of the FRs in polymer matrix. The images shown in Figure 7.16 indicate that all of the FRs were well dispersed in the furan resin matrix.

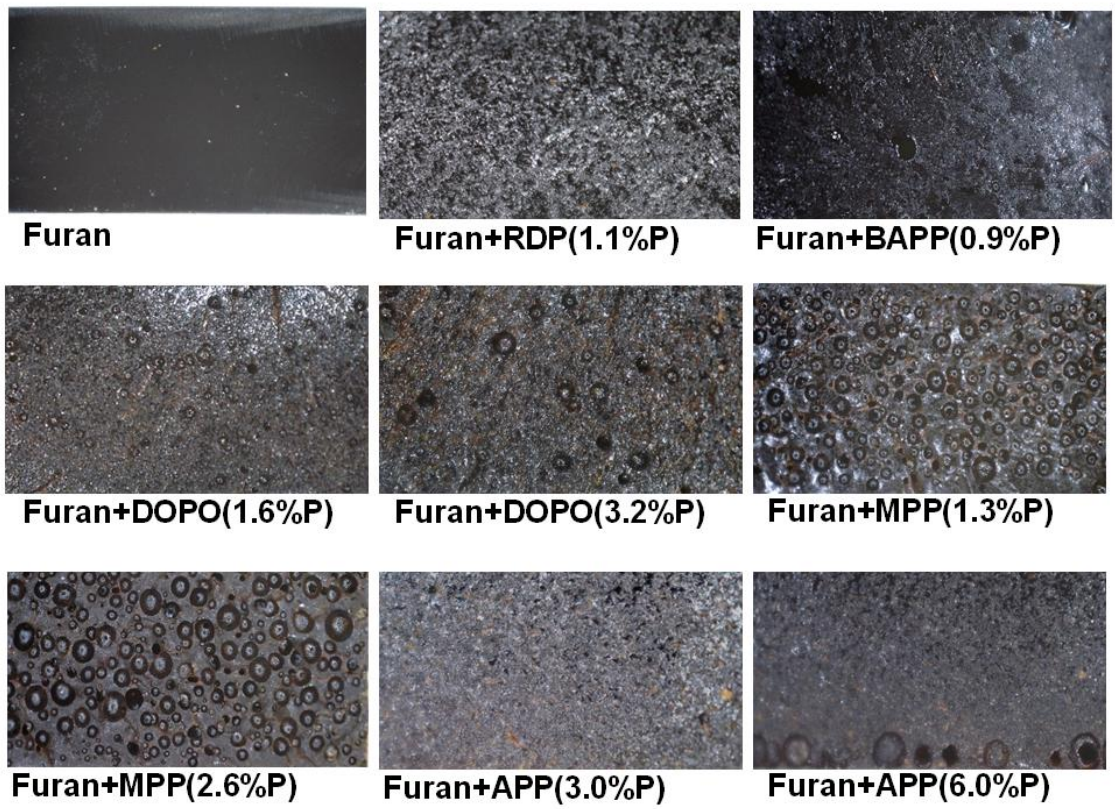

Figure 7.16: Optical images of cross-sections of control and flame retardant furan resins (50X magnification)

7.2.1 Flammability of flame retardant furan resins

The flammability of the FR-furan resin samples was evaluated by using LOI and UL-94 tests. The results are given in Table 7.13.

Table 7.13: LOI and UL-94 results of furan containing different flame retardants

Sample	LOI (%)	UL-94
Furan	39.4	V-0
Furan + RDP (1.1%P)	39.8	V-0
Furan + BAPP (0.9%P)	40.4	V-0
Furan + DOPO (1.6%P)	44.8	V-0
Furan + DOPO (3.2%P)	47.8	V-0
Furan + MPP (1.3%P)	56.8	V-0
Furan + MPP (2.6%P)	63.0	V-0
Furan + APP (3.0%P)	68.0	V-0
Furan + APP (6.0%P)	75.4	V-0

The LOI results reported in Table 7.13 show that furan resin has a LOI value of 39.4%, which is very high and the polymer is non-flammable. On addition of flame retardants the LOI increased further, Table 7.13. The increase in the LOI however, depended on the type of the flame retardant. On comparing the LOI values of different FR-furan resins in Table 7.13, APP is seen to be the most effective FR, as can be seen from the higher LOI values of Furan+APP samples in comparison to others, particularly Furan+APP(6.0%P) (75.4% LOI), followed by MPP and DOPO, respectively. BAPP and RDP were not effective in flame retarding furan resin as can be seen from their LOI values, which are similar to that of the control (Table 7.14). The high performance of Furan+APP sample was as expected from their high P content as compared to other flame retarded furan resins (Table 7.12). Since all FRs studied here are P based chemicals, their FR mechanisms of action are mainly related to a reaction between phosphorus reactive species, generated from FRs, and polymer [6,7], hence the flame retardant with higher percent P content provides better FR efficiency in comparison to the lower one, as can be seen from Figure 7.17 where LOI values as a function of % P are plotted. In UL-94 tests, the results show that all of the control and flame retarded furan resin samples passed with a V-0 rating in the vertical burning test, i.e. the samples did not ignite, which was as expected given their high LOI values, Table 7.13.

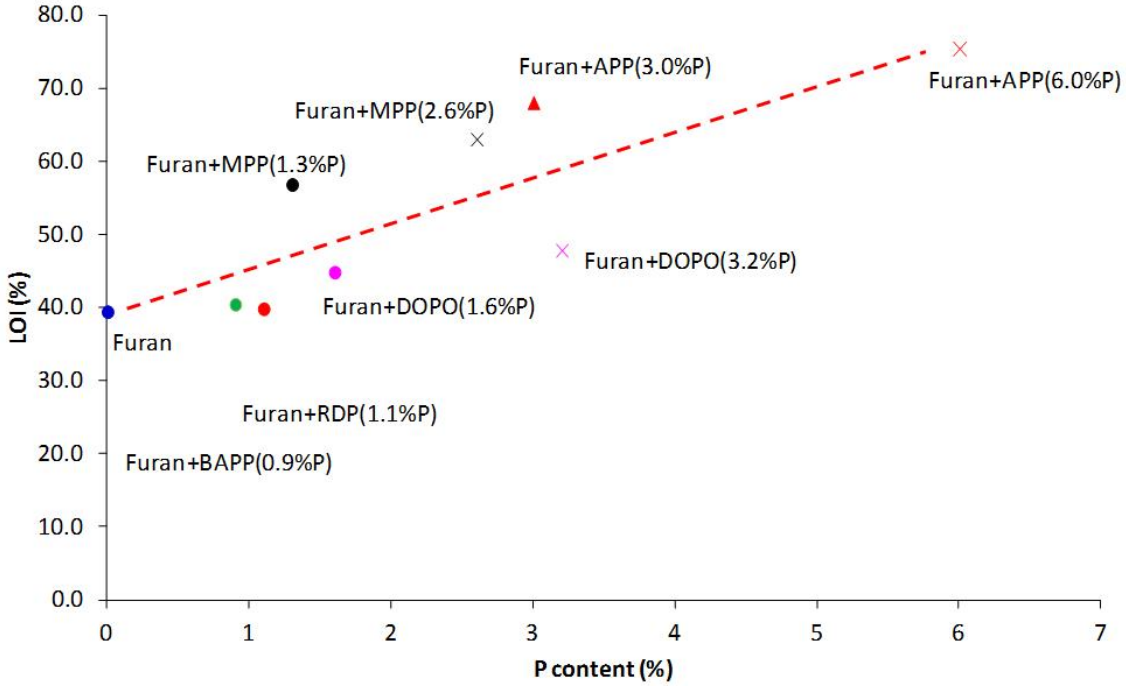

Figure 7.17: The 2-D plot of the LOI values of furan resin containing different flame retardants versus the P content in the samples

To have better understanding on the effect of the flame retardants on the flammability of furan resin, the cone calorimetric results of the control and flame retarded furan resin samples were also evaluated by using 50 kW/m^2 of external heat flux. The HRR, RSR and mass loss curve results are presented in Figure 7.18 and 7.19, respectively, and the results interpreted from these curves are given in Table 7.14.

Table 7.14: The cone calorimetric results of furan resin containing different flame retardants at 50 kW/m^2 heat flux

Sample	TTI (s)	T_{PHRR} (s)	PHRR (kW/m^2)	THR (MJ/m^2)	EHC (MJ/kg)	TSR (L)	Yield (%)	Fire rating parameters	
								FPI (s/(kW/m^2))	FIGRA ((kW/m^2·s)
Furan	52 ±2	73 ±2	489 ±21	24 ±1	12 ±1	47 ±21	46.7 ±0.2	0.11	6.7
Furan+RDP(1.1%P)	55 ±2	75 ±2	407 ±18	22 ±1	11 ±1	229 ±27	45.4 ±1.6	0.14	5.4
Furan+BAPP(0.9%P)	61 ±5	82 ±4	494 ±10	21 ±1	11 ±1	221 ±19	46.2 ±1.4	0.12	6.0
Furan+DOPO(1.6%P)	90 ±9	107 ±1	502 ±17	18 ±1	9 ±1	729 ±110	46.9 ±0.8	0.18	4.7
Furan+DOPO(3.2%P)	109 ±1	132 ±3	415 ±40	17 ±1	8 ±1	285 ±22	49.0 ±0.2	0.26	3.1
Furan+MPP(1.3%P)	70 ±3	85 ±1	160 ±76	9 ±4	6 ±2	10 ±7	51.3 ±0.1	0.44	1.9
Furan+MPP(2.6%P)	176 ±1	206 ±6	40 ±50	7 ±1	5 ±1	84 ±38	52.3 ±1.3	4.40	0.2
Furan+APP(3.0%P)	71 ±1	79 ±1	146 ±101	9 ±1	6 ±1	13 ±3	58.6 ±0.6	0.49	1.8
Furan+APP(6.0%P)	-	-	-	2 ±1	1 ±1	73 ±5	60.0 ±0.4	-	0.0

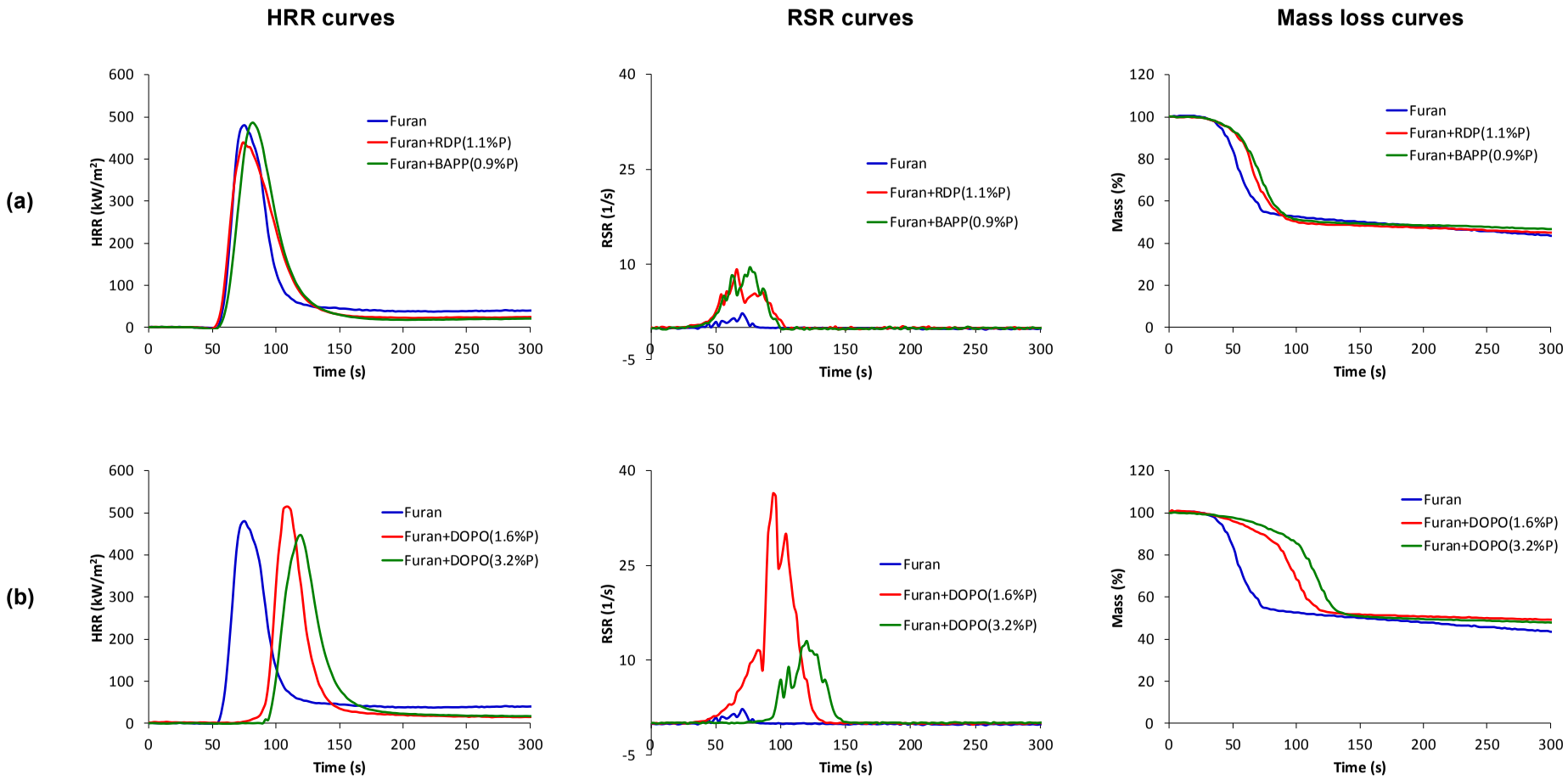

Figure 7.18: HRR, RSR, and mass loss curves as a function of time of (a) Furan+RDP(1.1%P) and Furan+BAPP(0.9%P), (b) Furan+DOPO(1.6%P) and Furan+DOPO(3.2%P) plaques tested at 50 kW/m^2 external heat flux

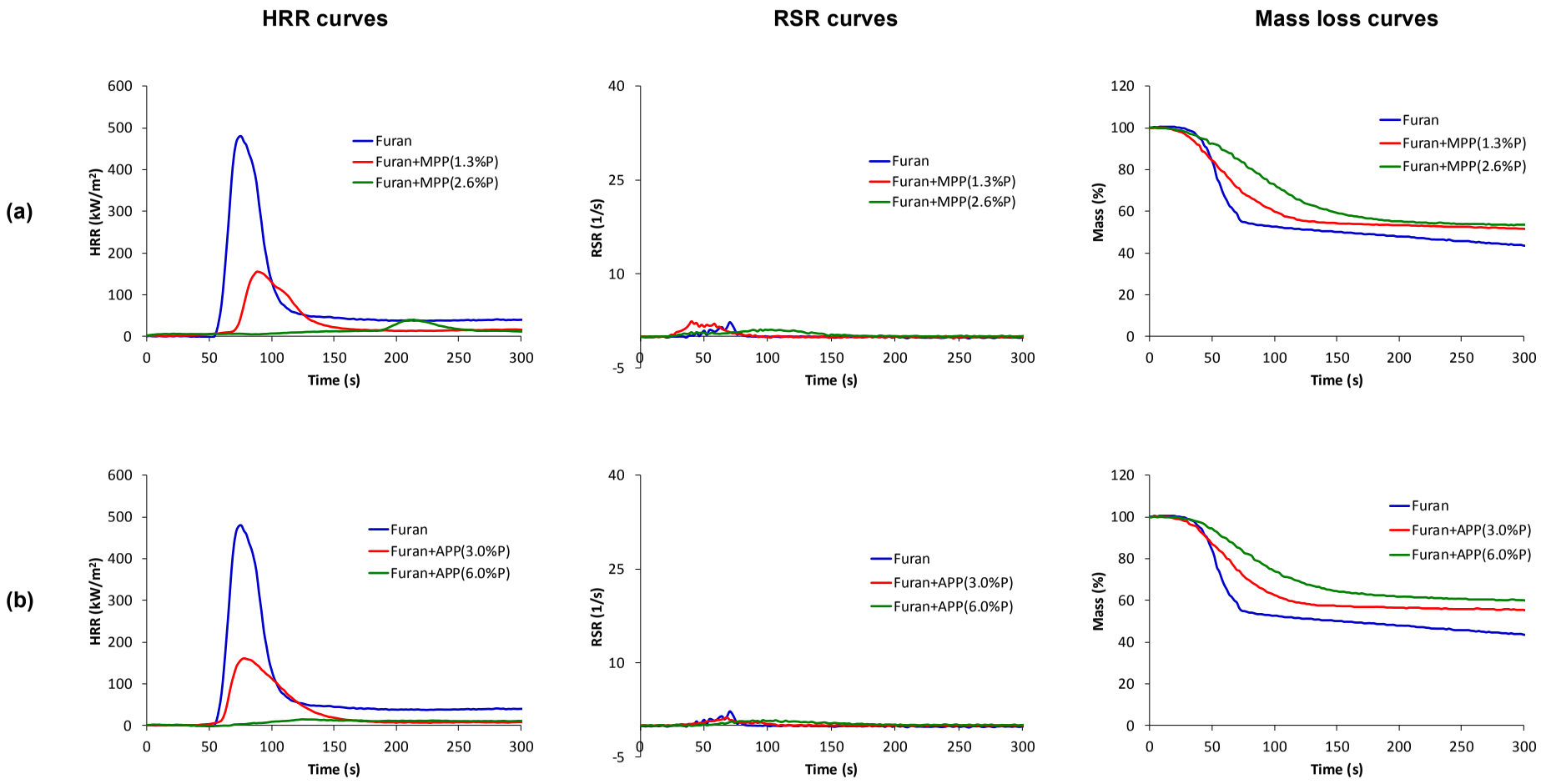

Figure 7.19: HRR, RSR, and mass loss curves as a function of time of (a) Furan+MPP(1.3%P) and Furan+MPP(2.6%P), (b) Furan+APP(3.0%P) and Furan+APP(6.0%P) plaques tested at 50 kW/m^2 external heat flux

The cone calorimetric results show that furan resin ignited at 52 s, and burned with PHRR of 489 kW/m^2 at 73 s. Furan resin produced 24 MJ/m^2 THR and 46.7% char residue. The total smoke released from furan resin was 47 L. With the presence of RDP (1.1% P content), there was a little effect on flammability as can be seen that the TTI of the furan resin was unaffected, the PHRR was reduced to 407 kW/m^2 PHRR, and THR reduced to 22 MJ/m^2. However, the smoke production of furan resin was increased from 47 L in the control to 229 L in Furan+RDP(1.1%P). For Furan+BAPP(0.9%P), the results show that BAPP increased the TTI slightly to 61 s, but did not show a clear effect on the PHRR as it burned with similar PHRR (494 kW/m^2) as observed in the control furan resin, Table 7.14. However, due to the shorter burning time of Furan+BAPP(0.9%P) (60 s) as compared to the control (74 s), Furan+BAPP(0.9%P) produced lower THR of 21 MJ/m^2. BAPP also increased the TSR of furan resin to 22 L, but did not affect the char formation as can be seen that the charred residue of Furan+BAPP(0.9%P) (46.2%) is similar to that of the control (46.7%). These results show that RDP and BAPP are not effective, as was also seen from LOI results.

In case of DOPO flame retardant, the addition of DOPO at 1.6% P content significantly delayed TTI of furan resin from 52 s to 90 s, but did not reduce the PHRR of the furan resin. The results in Table 7.14 show that after ignition although Furan+DOPO(1.6%P) burned with the similar PHRR as in the control, it burned for a shorter time (50 s), hence lower THR was produced in Furan+DOPO(1.6%P) (18 MJ/m^2) as compared to the control (24 MJ/m^2). The increase in TSR is also observed in Furan+DOPO(1.6%P), as compared to the control, Table 7.14. With the increase the content of DOPO to 3.2% P, the TTI was further increased to 109 s, and the PHRR was reduced to 415 kW/m^2. This therefore results in the lower THR of Furan+DOPO(3.2%P) (17 MJ/m^2) in comparison to the Furan+DOPO(1.6%P) (18 MJ/m^2). There was no effect on char formation.

The results for Furan resin containing MPP show that the MPP significantly improved the fire retardancy of the resin as it can be seen that at 1.3% P content MPP delayed the TTI of furan from 52 s to 70 s, and significantly decreased the PHRR of furan resin from 489 kW/m^2 to 160 kW/m^2 (~68% reduction). These results in a significant reduction in THR of Furan+MPP(1.3%P) sample (9 MJ/m^2) as compared to that of the control (24 MJ/m^2). Furan+MPP(1.3%P) also produced lower volume of smoke (10 L of TSR), and more charred residue (51.3%) in comparison to the control furan resin, Table 7.14. With the higher MPP content (2.6% P), there was further delay in TTI, i.e. from 70 s in Furan+MPP(1.3%P) to 176 s in Furan+MPP(2.6%P). After ignition, Furan+MPP(2.6%P) also burned with very low PHRR of 40 kW/m^2 at 206 s, producing 7 MJ/m^2 THR. The Furan+MPP(2.6%P) however did not show significant improvement in char formation as compared to Furan+MPP(1.3%P) as can be seen that the residue is slightly increased from 51.3% in Furan+MPP(1.3%P) to 52.3% in Furan+MPP(2.6%P).

The addition of APP at 3.0% P content increased the TTI of furan resin from 52 s to 71 s, and reduced the PHRR of furan resin by about 70%, i.e. from 489 kW/m^2 to 146 kW/m^2. Furan+APP(3.0%P) produced very low THR of 9 MJ/m^2, and a yield of charred residue of 58.6% in comparison to the control, Table 7.14. APP also reduced the TSR of furan resin from 47 L in the control to 13 L in Furan+APP(3.0%P). On increasing the APP content, the fire performance of Furan+APP was significantly improved as can be seen in that with the addition of APP at 6.0% P content there was no ignition.

The effective heat of combustion (EHC) results in Table 7.14 show that the EHC of furan resin (12 MJ/kg) was reduced with the presence of the flame retardants, indicating the improvement in fire performance of the sample. On comparing the EHC of furan resin containing different FRs, the results show that Furan+APP samples show the lowest EHC in comparison to others, followed by Furan+MPP, Furan+DOPO, Furan+BAPP and Furan+RDP, respectively, Table 7.14. To compare the hazards in a developing fire of these FR-furan samples, fire performance index (FPI) and FIGRA results are given in Table 7.14. The FPI results show that the fire hazard of furan resin was decreased with the addition of flame retardants as can be seen from the increase in FPI values in FR-furan samples as compared to the control. In comparison the efficiency of FRs, the results show the same trend as observed in the EHC, where APP and MPP were the most effective FRs to flame retard furan resin, seen from the higher FPI values in furan resin containing APP and MPP samples as compared to others, particularly Furan+APP(6.0%P) where the FPI could not be calculated as the sample did not ignite. A similar trend is also seen in the FIGRA results of control and flame retardant furan resin samples, where APP and MPP were the most effective FRs, as shown by the lower FIGRA values in Furan+APP and Furan+MPP samples in comparison to others, especially Furan+APP(6.0%P) where the lowest FIGRA (0 s/(kW/m^2)) is observed.

On comparing the relative overall fire performances of these FR-furan samples by plotting the total heat release (THR) against the fire growth rate values (PHRR/TTI) as presented in Figure 7.20, the results also show that Furan+APP and Furan+MPP were the most fire safe materials, shown by the lowest THR and fire growth rate as compared to others, followed by the Furan+DOPO, Furan+BAPP and Furan+RDP, respectively.

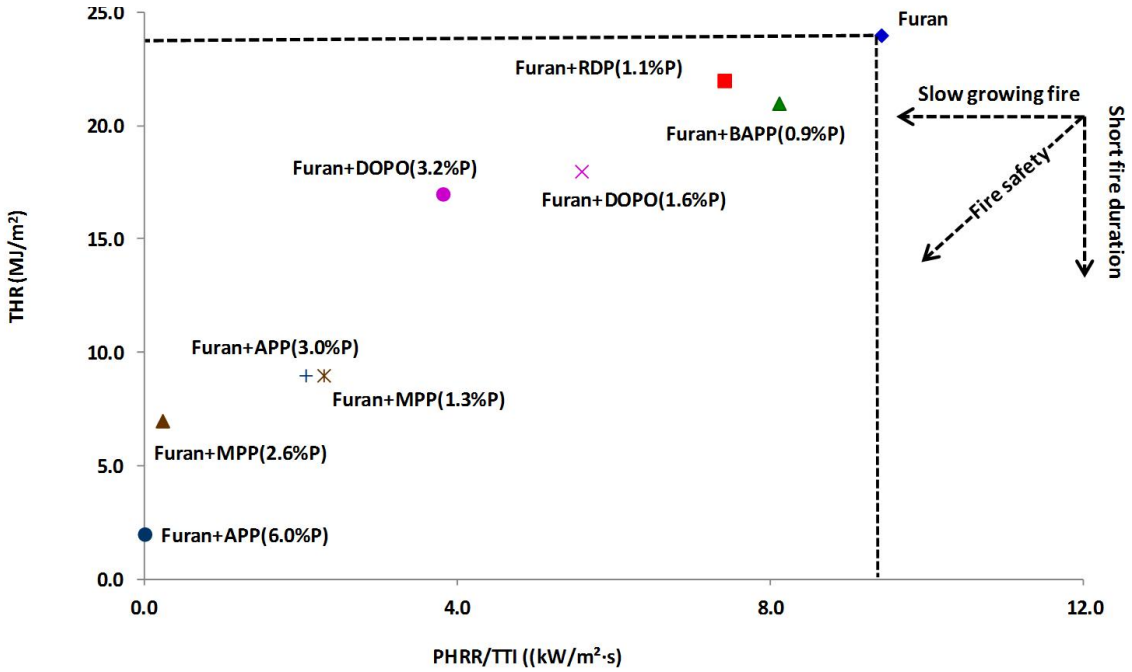

Figure 7.20: 2-D fire safety index of furan resin containing different P based flame retardants exposed to 50 kW/m^2 heat flux

From these cone calorimetric results, it therefore can be concluded that APP and MPP were the most effective FRs to enhance the fire performance of furan resin in comparison to other FRs as can be seen that with the addition of APP and MPP, the PHRR, THR and EHC of furan were significantly reduced, in particular the addition of APP at 6.0% P content prevented ignition.

7.2.2 Thermal decomposition of flame retardant furan resins

To better understand the mechanism of action of flame retardants the thermal decomposition behaviours of the control and flame retarded furan resins were studied from room temperature up to 900^{o}C in nitrogen and air. The TGA results of control and FR-furan samples in nitrogen and air are reported in Table 7.15 and 7.16, respectively, and some selective graphs are given in Figures 7.21 and 7.22. The results for all samples in both air and nitrogen show that there are small mass losses up to ~200^{o}C which can be attributed to the volatilisation of the absorbed moisture and/or solvent (i.e. water) present in the samples. Hence in the discussion of the thermal stability of these samples in the following section, the mass loss in this stage is not considered. In nitrogen, furan resin shows a single mass loss step between 168 – 845^{o}C with a mass loss of 47.4% and DTG max at 215^{o}C. While the TGA results in air show that furan resin decomposes with two main decomposition stages. The first step occurs between 183 - 541^{o}C with similar mass loss as observed in nitrogen (i.e. 47.9%), representing the main decomposition of furan [19,20]. Then the char formed in the first stage gradually decomposes further between 541 - 722^{o}C with the maximum rate of decomposition at 586^{o}C due to the thermo-oxidation of the char, leaving 0.7% residue at 900^{o}C.

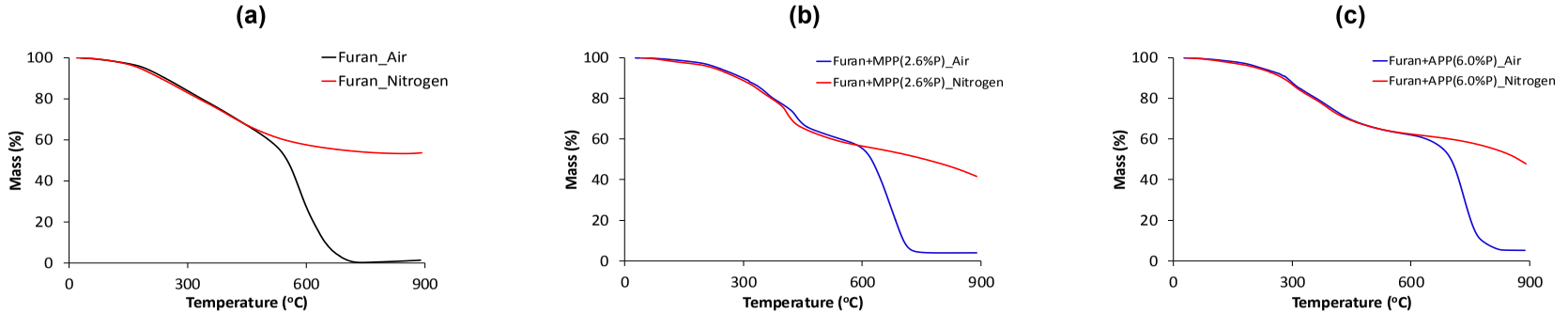

Figure 7.21: TGA curves of (a) Furan, (b) Furan+MPP(2.6%P)*, and (c)* Furan+APP(6.0%P) *in air and nitrogen*

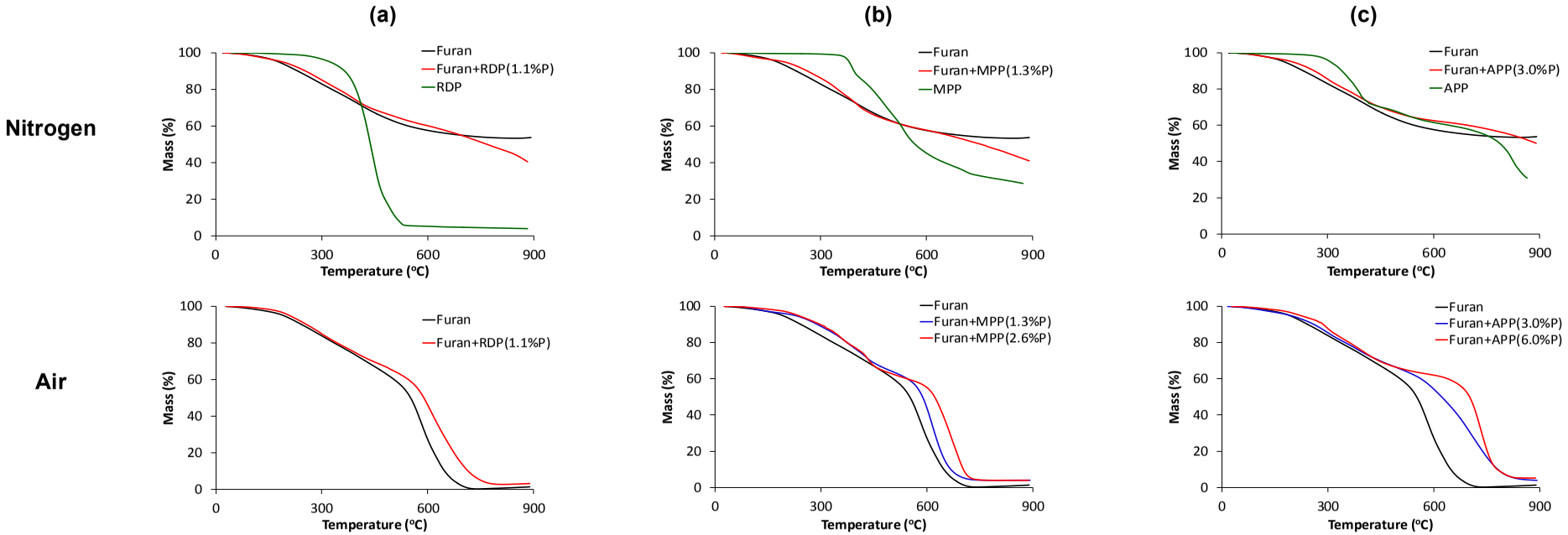

Figure 7.22: TGA curves of Furan and (a) Furan+RDP, (b) Furan+MPP and (c) Furan+APP in nitrogen and air

Table 7.15: TGA and DTG results of furan resin containing different P based flame retardants in nitrogen

Sample	Volatilisation of moisture/solvent			1st mass loss step			2nd mass loss step			Residue at 900°C (%)
	Temp range (°C)	Mass loss (%)	DTG Max (°C)	Temp range (°C)	Mass loss (%)	DTG Max (°C)	Temp range (°C)	Mass loss (%)	DTG Max (°C)	
Furan	RT – 168*	4.2	-	168 - 845	47.4	215	-	-	-	48.4
Furan+RDP(1.1%P)	RT – 170*	5.3	-	170 - 553	37.7	380	553 - 900	21.5	-	35.5
Furan+BAPP(0.9%P)	RT – 177*	4.3	-	177 - 630	39.8	380	630 - 900	31.9	-	24.0
Furan+DOPO(1.6%P)	RT – 183*	5.1	-	183 - 608	36.7	283	608 - 900	24.3	-	33.9
Furan+DOPO(3.2%P)	RT – 207*	4.9	-	207 - 642	33.6	316	642 - 900	22.6	-	38.9
Furan+MPP(1.3%P)	RT – 203*	5.3	-	203 - 597	37.1	348	597 - 900	16.7	-	40.9
Furan+MPP(2.6%P)	RT – 198*	4.7	-	198 - 603	39.1	410	603 - 900	14.7	-	41.5
Furan+APP(3.0%P)	RT – 196*	4.7	-	196 - 614	33.2	394	614 - 900	12.1	-	50.0
Furan+APP(6.0%P)	RT – 198*	4.9	-	198 - 690	34.9	390	690 - 900	12.3	-	47.9

Note: RT represents room temperature, * = Onset of decomposition temperature

Table 7.16: TGA and DTG results of furan resin containing different P based flame retardants in air

Sample	Volatilisation of moisture/solvent			1st mass loss step			2nd mass loss step			Residue at 900°C (%)
	Temp range (°C)	Mass loss (%)	DTG Max (°C)	Temp range (°C)	Mass loss (%)	DTG Max (°C)	Temp range (°C)	Mass loss (%)	DTG Max (°C)	
Furan	RT – 183*	2.5	-	183 – 541	47.9	226	541 - 722	48.9	586	0.7
Furan+RDP(1.1%P)	RT – 177*	2.7	-	177 – 563	40.2	296	563 - 735	53.9	610	3.2
Furan+BAPP(0.9%P)	RT – 175*	2.5	-	175 – 559	42.8	375	559 - 793	51.9	593	2.8
Furan+DOPO(1.6%P)	RT – 170*	2.7	-	170 – 596	39.4	261	596 - 882	53.3	715	4.6
Furan+DOPO(3.2%P)	RT – 186*	2.9	-	186 – 615	35.0	276	615 - 890	52.0	700	9.1
Furan+MPP(1.3%P)	RT – 204*	3.3	-	204 – 552	37.1	341	552 - 707	55.7	595	3.9
Furan+MPP(2.6%P)	RT – 198*	3.1	-	198 – 596	39.5	344	596 - 737	53.3	656	7.2
Furan+APP(3.0%P)	RT – 210*	3.0	-	210 – 574	34.0	389	574 - 843	59.0	703	4.0
Furan+APP(6.0%P)	RT – 204*	2.7	-	204 - 690	35.7	408	690 - 840	46.4	734	5.2

Note: RT represents room temperature, * = Onset of decomposition temperature

On comparing the TGA results of FR-furan samples in nitrogen and air (Figure 7.21), a similar behaviour to that observed in the control furan resin is seen where the results show that the first decomposition step of the samples in air is similar to that in nitrogen, representing the decomposition of the sample. A difference is seen only in the second mass loss stage as the results in air show higher mass loss due to the thermal oxidation of the char formed in the first step. On addition of RDP flame retardant, the TGA results in nitrogen show that RDP did not affect the onset of decomposition temperature, but reduced the mass loss in the first mass loss step, which is related to the decomposition of furan resin, as it can be seen that in the first mass loss step Furan+RDP(1.1%P) decomposes between 170 – 553^{o}C with smaller mass loss (37.7%) than in the control (47.4%). However, there is further decomposition up to 900^{o}C as can be seen from Figure 7.22. Furan+RDP(1.1%P) produces 35.5% residue at the end of its decomposition in nitrogen. In air, the RDP did not affect the onset of decomposition temperature of furan, but extended the temperature range of the first decomposition step of furan from RT – 541^{o}C to RT - 563^{o}C with a slightly smaller mass loss of 40.2% as compared to the control (47.9%). The second mass loss step, related to the oxidation of the char, show that RDP also improved the oxidation resistance of the char as can be seen that the DTG max in the second decomposition step of Furan+RDP(1.1%P) (610^{o}C) is at higher temperature than the control (586^{o}C), and also more charred residue at 900^{o}C is obtained in Furan+RDP(1.1%P) (3.2%) as compared to the control (0.7%).

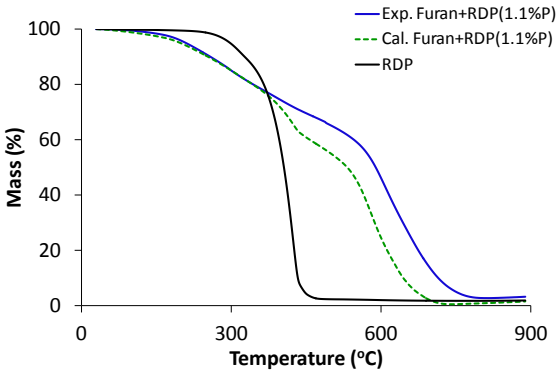

Figure 7.23: The experimental and calculated TGA curves of Furan+RDP(1.1%P) in air atmosphere

This improvement could be explained by the reaction between an aryl phosphonic acid, generated from RDP, and furan resin during the decomposition as can be seen from the difference between the experimental and calculated TGA curves of Furan+RDP(1.1%P) where the experimental curve shows the higher mass residue than the calculated one after 360^{o}C where the RDP readily decomposes, Figure 7.23. On heating, RDP decomposes and produces an aryl phosphonic acid which could then work as a Lewis acid to catalyse the char formation of the polymer during decomposition [6,21-23], resulting in the lower mass loss and higher char residue, as compared to the control. As lower mass loss implies fewer volatiles being produced, and better char formation, the flammability of Furan+RDP(1.1%P) was therefore lower than the control. However, on comparing with the control furan resin, the improvement in the thermal stability of Furan+RDP(1.1%P) was not significant (Table 7.16), hence only a marginal increase

in the fire retardancy of Furan+RDP(1.1%P) was observed as can be seen from the only small increase in the LOI (Table 7.13), and marginal reduction in the THR and EHC in Furan+RDP(1.1%P) (Table 7.14) as compared to the control.

The results in nitrogen show that the presence of BAPP at 0.9% P content slightly increased the onset of decomposition temperature of furan resin from 168°C in the control to 177°C, and DTG max in the first mass loss step from 215°C in to control to 380°C in Furan+BAPP(0.9%P). BAPP also shows slightly reduced mass loss in the first step of furan (47.4%) to 39.8% in Furan+BAPP(0.9%P). In the second mass loss step, Furan+BAPP(0.9%P) decomposes further due to the decomposition of BAPP at high temperature, with 31.9% mass loss, giving 24.0% residue at 900°C. In air, Furan+BAPP(0.9%P) shows similar decomposition in the first mass loss step as in nitrogen and it can be seen that BAPP significantly increased the DTG max in the first step of furan resin from 226°C to 375°C, and reduced the mass loss in the first step of furan resin from 47.9% to 42.8%. Hence, this can explain the increase in the TTI and T_{PHRR} of Furan+BAPP(0.9%P) in comparison to the control in cone calorimetry tests (Table 7.14), as the TGA results show that Furan+BAPP(0.9%P) decomposes at higher temperature with lower mass loss than the control. In the second mass loss step, Furan+BAPP(0.9%P) decomposes more rapidly in air as compared to that in nitrogen, which is due to the oxidation of the char. The second mass loss step in air of Furan+BAPP(0.9%P) occurs between 559 – 793°C, producing higher charred residue of 2.8% at 900°C in comparison to the control (0.7%). These results were as expected from the FR activity of BAPP in the condensed phase as it also produces aryl phosphonic acid upon its decomposition [21,23], hence is expected to improve the thermal stability of furan by increasing the char formation tendency of furan resin due to the chemical reaction between the produced aryl phosphonic acid and furan resin in the similar manner as discussed for Furan+RDP(1.1%P) above. The discussion is supported by the comparison between the experimental and calculated TGA curves as presented in Figure 7.24.

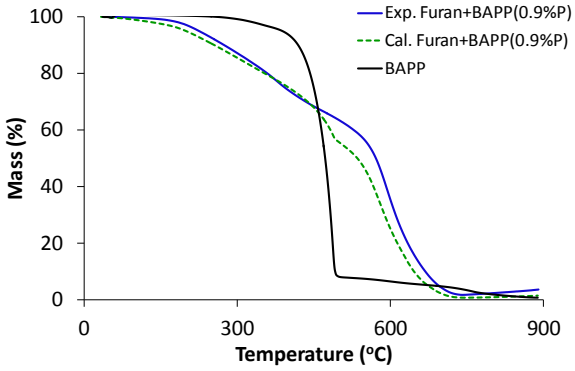

Figure 7.24: The experimental and calculated TGA curves of Furan+BAPP(0.9%P) in air atmosphere

The results show that after 460°C where the main decomposition of BAPP takes place the experimental curve shows better thermal stability than the calculated due to the reaction between the aryl phosphonic acid, produced from the pyrolysis of BAPP, and furan resin that leads to more char formation. Hence, because of the improved thermal stability of

Furan+BAPP(0.9%P), it exhibits lower flammability as compared to the control as discussed in *Section 7.2.1*.

With the addition of DOPO, the TGA in nitrogen show that DOPO improved the thermal stability of furan resin by reducing the mass loss during the decomposition of furan resin as can be seen from the fact that Furan+DOPO(1.6%P) decomposes between 183 - 608^{o}C in the first mass loss step, showing lower mass loss of 36.7% in comparison to the control (47.4%). Similar to furan resin containing RDP and BAPP, the decomposition occurs between 608 - 900^{o}C giving 33.9% charred residue at the end. In air, Furan+DOPO(1.6%P) shows similar decomposition behaviour in the first mass loss step as in nitrogen, as the addition of DOPO in furan resin improved the thermal stability of furan resin by reducing the rate of decomposition in the first step of furan resin as can be seen that the first decomposition step of Furan+DOPO(1.6%P) occurred in a broader range of temperature (170 - 596^{o}C) with the lower mass (39.4%) as compared to the control, Table 7.16. The results in air also show that DOPO improved the char formation of the furan resin significantly as can be seen from the higher charred residue was observed in Furan+DOPO(1.6%P) (4.6%) compare to the control (0.7%). This again could be explained by the condensed phase activity of DOPO [21], which is a P based flame retardant, to increase the char formation tendency of furan resin due to the reaction between the reactive phosphorus species from FRs and polymer as can be seen from the difference between the experimental and calculated curves in Figure 7.25.

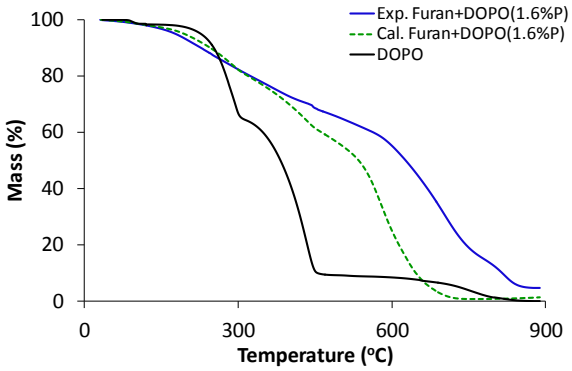

Figure 7.25: The experimental and calculated TGA curves of Furan+DOPO(1.6%P) in air atmosphere

On comparing the results of Furan+DOPO(1.6%P) with others (i.e. Furan+RDP(1.1%P) and Furan+BAPP(0.9%P)) discussed above, DOPO was more effective in improving the thermal stability of furan resin as the Furan+DOPO(1.6%P) decomposed over a broader range of temperature with smaller mass loss in the first decomposition step, and produced more char residue at the end. As a result of higher thermal stability of Furan+DOPO(1.6%P), it exhibits lower flammability as compared to Furan+RDP(1.1%P) and Furan+BAPP(0.9%P), Table 7.14. The higher efficiency of DOPO as compared to RDP and BAPP can be explained in two possible ways. The first is related to the decomposition of DOPO which occurs at a relatively low temperature (Figure 7.25) compared to that of RDP and BAPP, hence the reactive phosphorus species produced from DOPO possibly reacts with furan resin before or at a similar

temperature as the maximum rate of decomposition temperature (DTG max) of furan resin. This therefore results in the low mass loss in the first decomposition step of Furan+DOPO(1.6%P) in comparison to others, i.e. Furan+RDP(1.1%P) and Furan+BAPP(0.9%P), as the decomposition of furan resin was retarded in the early stages. The second is possibly due to the high P content in Furan+DOPO (1.6% P content) as compared to the others, i.e. 1.1% P in Furan+RDP and 0.9% P in Furan+BAPP, hence more reactive phosphorus species were produced to react with furan, hence resulting in the higher efficiency of DOPO.

Furan+MPP(1.3%P) decomposes with two mass loss steps in nitrogen. The first occurs between 203 and 597^{o}C, showing smaller mass loss (37.1%) than the control with the DTG max at 348^{o}C. Furan+MPP(1.3%P) then decomposes further up to 900^{o}C due to the decomposition of MPP at high temperature (Figure 7.22), producing 40.9% residue at the end. In air, Furan+MPP(1.3%P) also shows two stages of decomposition occurring between 204 and 552^{o}C with a mass loss of 37.1%, followed by the second step which is related to the char oxidation between 552 and 707^{o}C producing 3.9% residue at the end of decomposition. In comparison to the control, the TGA results, particularly in air, show that the addition of MPP reduces the mass loss in the first decomposition step of furan resin from 47.9% to 37.1% (~ 23% reduction), and increases the residue at end of decomposition of furan resin from 1.4% to 3.9%. The improvement in the thermal stability of Furan+MPP(1.3%P) in comparison to the control can be explained by the condensed phase activity of MPP as on heating MPP releases phosphoric acid to react with furan resin, which results in the increase in the char formation tendency of the furan resin. The effect is seen more clearly when comparing the experimental curve to the calculated one in Figure 7.26, where the experimental curve shows lower mass loss during the decomposition compared to the calculated one, suggesting the reaction between MPP and furan resin increased the char formation of the Furan+MPP(1.3%P) sample.

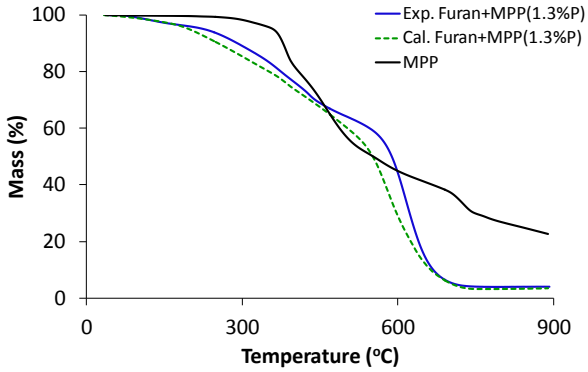

Figure 7.26: The experimental and calculated TGA curves of Furan+MPP(1.3%P) in air atmosphere

On comparing with other FR-furan samples discussed above, this shows that MPP improved the thermal stability of furan in a similar manner as RDP, BAPP, and DOPO by increasing the char formation of furan resin, and the performance of MPP was more pronounced than others, as shown by the lower mass loss in the first mass step and relatively high charred residue as compared to others. This is due to the synergistic effect between phosphorus (P) and nitrogen

(N) in MPP flame retardant [24]. In the presence of a N compound, the P based flame retardant can form the P-N bonded intermediates which are more reactive than P based flame retardants without the nitrogen, resulting in faster rate of char formation [6,24]. This therefore leads to the significant improvement in fire retardancy of Furan+MPP(1.3%P) as compared to the control as can be seen from the high LOI value, and significant reduction in the PHRR, THR, and EHC of Furan+MPP(1.3%P) in comparison to the control.

For APP, which is another P-N containing flame retardant, the TGA results in nitrogen show that Furan+APP(3.0%P) decomposes between 196 and 614^{o}C with relatively low mass loss of 33.2% in comparison to the control (47.4%), followed by a second decomposition step between 614 and 900^{o}C, producing charred residue of 50.0% at 900^{o}C. This shows that the presence of APP improves the thermal stability of furan resin, particularly in the first mass loss step, by reducing the mass loss of furan resin during the decomposition. The FR performance of APP is also seen from the TGA results in air (Table 7.16) as Furan+APP(3.0%P) decomposes between 210 – 574^{o}C in the first decomposition step, showing low mass loss (34.0%) and the high DTG maximum (389^{o}C) in comparison to the control furan resin. This is followed by the char oxidation stage occurred between 574 and 843^{o}C with the DTG maximum at 703^{o}C, producing more charred residue (4.0%) than the control (0.7%) at the end of decomposition. In comparison to other FR-furan samples, these results show that the thermal stability of Furan+APP(3.0%P) was higher as can be seen from its relatively low mass loss, and significantly higher DTG maximum in comparison to others (Table 7.16). Because of the significantly better thermal stability of Furan+APP(3.0%P), it therefore exhibit lowest flammability in comparison to others as can be seen from the flammability results discussed in *Section 7.2.1*. The high performance of APP could arise from a P-N synergistic effect and the high P content of APP flame retardant, in particular the latter as can be seen that the P content on Furan+APP(3.0%P) was significantly higher than others (Table 7.12), hence, on heating, more phosphorus reactive species, i.e. phosphoric acid, are released. This results in more reaction between phosphoric acid and furan, leading to the significant improvement in the char formation of Furan+APP(3.0%P) as can be seen from the significant difference between the experimental and calculated TGA curves of Furan+APP(3.0%P), particularly in the second mass loss step which is related to the char oxidation of the sample, Figure 7.27.

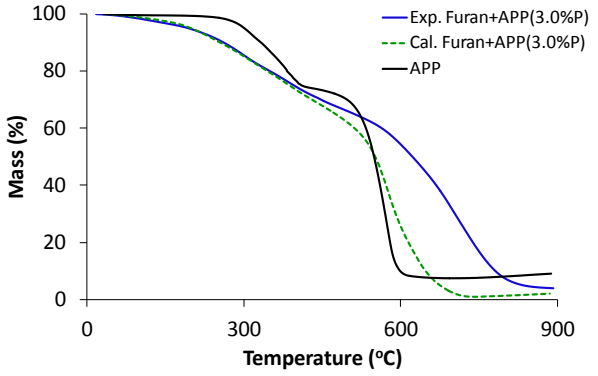

Figure 7.27: The experimental and calculated TGA curves of Furan+APP(3.0%P) in air atmosphere

7.3 Conclusions

For PLA, three flame retardants including NP, OP and ZP flame retardants were used. The results show that NP and OP flame retardants were the most effective flame retardants. With 1% P level in each FR system V-0 rating could be achieved. Hence they were selected for producing the FR-PLA fibres. Only PLA+OP could be extruded into filaments, and the maximum OP content that could be processed was 2% P level (8.4% solid content). Based on these results, OP flame retardant with good processability was also used for producing FR-PP fibres. The flammability results of PP+OP samples show that OP flame retardant was less effective in PP than in PLA. With 1 and 2% P content only V-2 rating could be achieved in a UL-94 test. The fibre extrusion of PP+OP samples was explored to identify the maximum OP content on PP that could be processed into filaments. The results showed that OP flame retardant at 1% P level (4.2% solid content) was the maximum that could be processed. Above this level the viscosity of the molten polymer was too low to process. From these, the optimised FR formulations of PLA+OP(2%P) and PP+OP(1%P) were therefore selected for producing flame retardant PLA and PP fibres to be used for natural fibre composites.

The furan resin showed very low flammability and a V-0 rating in the UL-94 test could be achieved. Out of a number of different P based flame retardants studied, the addition of APP and MPP were seen to be most effective in comparison to others, as these significantly increased the LOI value of furan resin, and reduced the PHRR, THR and EHC of furan resin by more than 50% in cone calorimetric results. Based on these results, furan resin containing APP and MPP were selected to be used as FR polymer matrix for producing flame retardant natural fibre composites in the following chapter.

7.4 References

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Chapter 8: Development of FR composites by using different combinations of FR components

This chapter discusses the effect of combining different flame retardant (FR) treated components on the fire and mechanical performance of the derived natural fibre composites. The reinforcing component used here was woven fabric of flax fibre treated with guanylurea methylphosphonate (GUP) employing the optimised formulation developed in *Chapter 5*. Polymer matrices were either thermoplastic: flame retardant polypropylene (PP-FR) and polylactic acid (PLA-FR), or flame retarded poly(furfuryl alcohol) (furan-FR). Based on the results in *Chapter 7*, commercially available organophosphorus based flame retardant (OP) at 1 and 2% P content was chosen to render PP and PLA flame retardant, while ammonium polyphosphate (APP) and melamine polyphosphate (MPP) were chosen for furan-FR. The effect of these components on the fire and mechanical performances of derived natural fibre composites are studied. The contents of this chapter are divided into two sections based on types of polymer, thermoplastic: flax reinforced polypropylene (flax/PP) and polylactic acid (flax/PLA); and flax reinforced poly(furfuryl alcohol) (flax/furan).

8.1 Flame retardant flax/PP and flax/PLA composites

In order to study the effect of FR components on fire and mechanical properties of flax/PP and flax/PLA composites, FR polymer matrices were prepared by melt-pressing PP and PLA containing OP flame retardant at 1 and 2% P level into polymer films. Since it is difficult to align continuous filaments (*Chapter 7*) in a composite, it was decided to make polymer films, which can be used as alternate layers with flax fabrics in a composite structure. Since composition and processing conditions are similar for these fibres and polymer films, hence from these composites behaviour of flame retardant fibres can be established. Flax fabrics were treated with GUP flame retardant to obtain FR reinforcement with GUP content of 0.75, 1.0, 1.5, and 2.0% P level on the fabrics. The composites laminates were prepared by melt-pressing stacked layers of these control/FR treated flax fabrics and control/FR containing polymer films by using different combinations of FR components, as shown in Table 8.1. The stacking arrangement included placing six layers of control/FR flax fabric between seven layers of control/FR polymer films, the latter being outside on both surfaces. This was to ensure that the outer surfaces of composites were covered with polymer matrix when melt-pressing into laminates. The mass fraction between flax and polymer was adjusted at 50/50 wt-% in all samples.

Table 8.1: Sample composition for control and flame retarded flax/PP and flax/PLA laminates (50/50 wt-%)

Sample	Reinforcement	Polymer matrix	P Cont. on composite (%)
Flax/PP	Flax	PP	-
Flax/PP-FR(1%P)	Flax	PP+OP(1%P)	0.5
Flax/PP-FR(2%P)	Flax	PP+OP(2%P)	1.0
Flax-FR(2%P)/PP	Flax+GUP(2%P)	PP	1.0
Flax-FR(1%P)/PP-FR(1%P)	Flax+GUP(1%P)	PP+OP(1%P)	1.0
Flax/PLA	Flax	PLA	-
Flax/PLA-FR(1%P)	Flax	PLA+OP(1%P)	0.5
Flax/PLA-FR(2%P)	Flax	PLA+OP(2%P)	1.0
Flax-FR(1.5%P)/PLA	Flax+GUP(1.5%P)	PLA	0.75
Flax-FR(0.75%P)/PLA-FR(1%P)	Flax+GUP(0.75%P)	PLA+OP(1%P)	0.88

8.1.1 Fire performance of flame retardant flax/PP and flax/PLA composites

The fire performance of the prepared control and flame retardant flax/PP and flax/PLA laminates were evaluated by using UL-94 and cone calorimetry (35 kW/m^2 heat flux) techniques.

Flax/PP composites

The UL-94 results of flax/PP composites reported in Table 8.2 show that control flax/PP failed vertical rating test as the sample completely burned up to the sample holder. The rate of burning was 116.9 mm/min. In horizontal orientation it burned slowly up to the sample holder with rate of burning of 18.1 mm/min.

Table 8.2: UL-94 results of control and flame retardant flax/PP composites

Sample	Horizontal burning rate (mm/min)	Vertical burning rate (mm/min)	V-Rating
Flax/PP	18.1 ±0.9	116.9 ±12.0	Failed
Flax/PP-FR(1%P)	12.8 ±1.1	98.7 ±1.8	Failed
Flax/PP-FR(2%P)	11.4 ±0.6	82.5 ±5.7	Failed
Flax-FR(2%P)/PP	-*	55.0 ±6.3	Failed
Flax-FR(1%P)/PP-FR(1%P)	-*	51.9 ±4.4	Failed

* The flame extinguished before reaching timing mark

With the use of flame retardant polypropylene (PP-FR) matrix alone, the results show that Flax/PP-FR(1%P) with 0.5% P content also failed the vertical rating test, and burned with rates of burning of 98.7 and 12.8 mm/min in vertical and horizontal orientations, respectively. The increase in FR content on PP-FR matrix to 2% P also did not show significant improvement in flammability of flax/PP as Flax/PP-FR(2%P) only shows slightly lower rates of burning than Flax/PP-FR(1%P) in both vertical and horizontal orientations, but still failed the vertical rating

test as seen from Table 8.2. The use of FR treated flax fabrics to prepare flax/PP composites shows better improvement in flammability of flax/PP as can be seen that Flax-FR(2%P)/PP although failed the vertical rating, it burned with much lower vertical rate of burning (55.0 mm/min, i.e. > 50% reduction), as compared to the control (116.9 mm/min), and a horizontal rate of burning could not be calculated as the flame extinguished before reaching the timing mark. With the use of FR components in both polymer matrix and reinforcement of flax/PP composite, Flax-FR(1%P)/PP-FR(1%P) shows similar performance as observed in Flax-FR(2%P)/PP, i.e. it failed the vertical rating test as the sample completely burned with the rate of burning of 51.9 mm/min, and a horizontal rate of burning could not be calculated.

The flammability of the control and flame retardant flax/PP composites evaluated by using calorimetry at 35 kW/m^2 are presented in Figure 8.1, and the derived results are reported in Table 8.3. The results show that flax/PP composite ignited at 49 s, and burned with two peaks of HRR of 516 kW/m^2 at 101 s and 351 kW/m^2 at 159 s, producing 88 MJ/m^2 THR. As already discussed in detail in *Chapter 5*, the burning behaviour with two peaks of PHRRs is commonly seen in natural fibre reinforced composites as on heating the composite the appearance of the first PHRR represents the burning of the composite after ignition. During this stage the flax fibres start charring, and then form a charred layer that acts as a thermal barrier for the underlying polymer, slowing down its burning until the charred layer cracks and then the second peak appears [1]. The control flax/PP shows 23 MJ/kg EHC and 9.1% charred residue. With the presence of OP flame retardant in PP matrix, Flax/PP-FR(1%P) shows small increase in TTI (53 s) in comparison to the control (49 s), but lower PHRRs with 378 kW/m^2 at 91 s in the first peak, and 316 kW/m^2 at 154 s in the second peak. However, Flax/PP-FR(1%P) burned for slightly longer time than control flax/PP, Figure 8.1, hence showing only a small reduction in its THR (86 MJ/m^2) compared to the control (88 MJ/m^2). There was no effect on char formation, i.e. 9.9% as compared to 9.1% in the control. With the increase of OP content in the matrix of composites to 2% P, the results show that there is no further improvement in the flammability of the composites, as can be seen that Flax/PP-FR(2%P) shows similar results to those observed in Flax/PP-FR(1%P) for all parameters, Table 8.3.

Table 8.3: Cone calorimetric results of control and flame retardant flax/PP composites at 35 kW/m^2

Sample	TTI	1st Peak		2nd Peak		THR	EHC	TSR	Char
	(s)	T_{PHRR} (s)	PHRR (kW/m^2)	T_{PHRR} (s)	PHRR (kW/m^2)	(MJ/m^2)	(MJ/kg)	(L)	(%)
Flax/PP	49 ±2	101 ±4	516 ±43	159 ±4	351 ±36	88 ±1	23 ±1	764 ±18	3.1 ±0.2
Flax/PP-FR(1%P)	53 ±2	91 ±4	378 ±11	154 ±14	316 ±8	86 ±5	22 ±2	1120 ±62	3.9 ±0.5
Flax/PP-FR(2%P)	53 ±1	92 ±3	369 ±2	166 ±25	327 ±21	86 ±2	22 ±1	1480 ±166	4.1 ±0.7
Flax-FR(2%P)/PP	150 ±1	191 ±1	384 ±68	263 ±4	448 ±4	102 ±3	22 ±1	2228 ±415	19.5 ±3.5
Flax-FR(1%P)/PP-FR(1%P)	77 ±3	98 ±3	263 ±55	144 ±14	240 ±4	78 ±9	20 ±1	1301 ±248	18.4 ±0.9

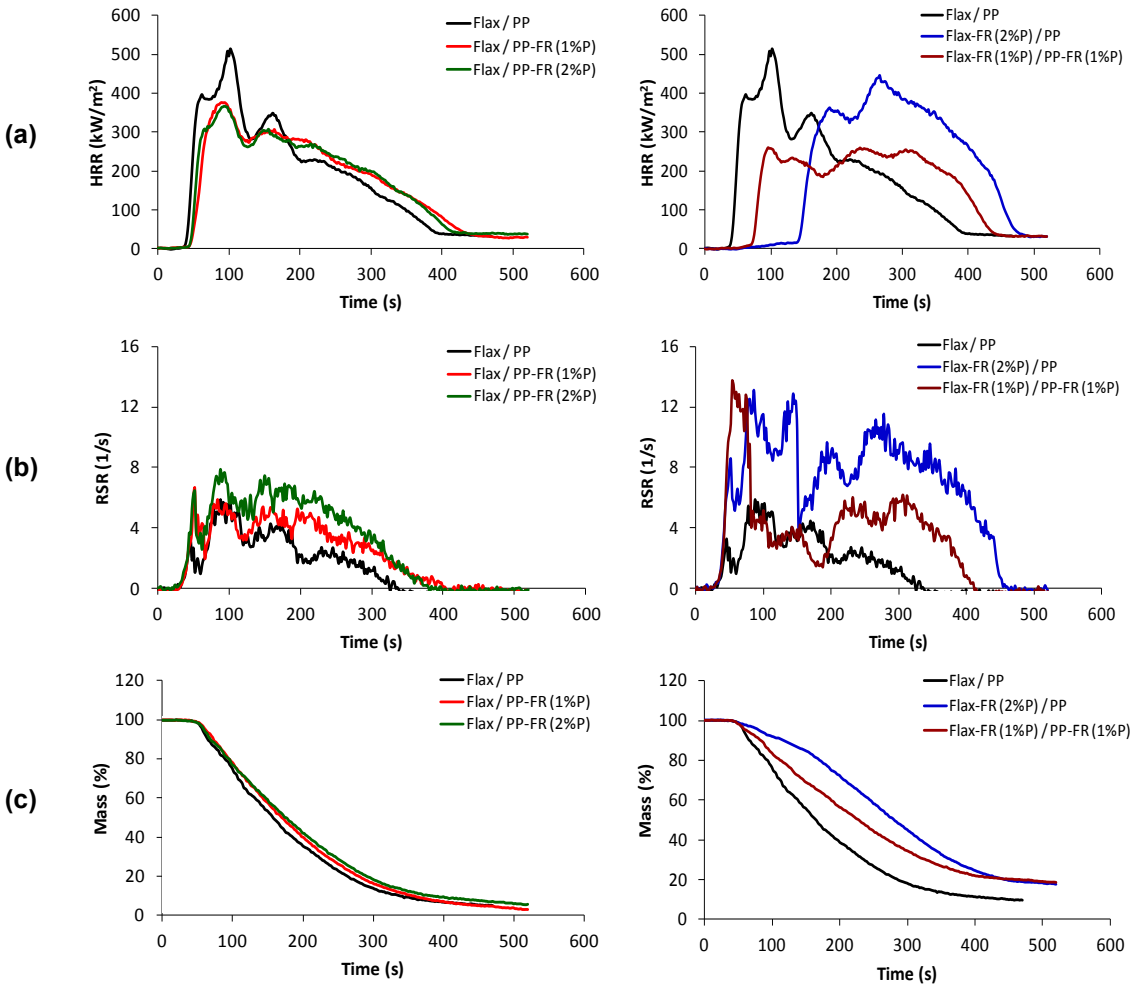

Figure 8.1: Cone calorimetric results of control and flame retardant flax/PP composites at 35 kW/m^2: (a) HRR, (b) RSR, and (c) mass loss curves as a function of time

With the use of GUP flame retardant on the flax component of the flax/PP composite, Flax-FR(2%P)/PP shows significant delay in TTI (150 s) in comparison to the control (49 s). Flax-FR(2%P)/PP burned with lower PHRR than the control with 384 kW/m^2 in the first peak, but higher (448 kW/m^2) in the second peak. The results in Figure 8.1 show that Flax-FR(2%P)/PP also burned for much longer time than the control, hence producing higher THR (102 MJ/m^2) than the control (88 MJ/m^2). Flax-FR(2%P)/PP shows significant improvement in char formation (19.5%) in comparison to the control (9.1%), which was as expected from the condensed phase activity of GUP flame retardant as discussed in *Chapter 5*. In comparison to the flame retardant flax/PP prepared from the FR matrix component (i.e. PP+OP), these results show that the use of GUP flame retardant on flax show significant improvement in TTI and char formation, but is slightly less effective in reducing PHRRs of the composites. The use of flame retardant flax and flame retardant PP components in Flax-FR(1%P)/PP-FR(1%P) laminate shows relatively high TTI of 77 s, with the significant reduction in both PHRR values in comparison to the control. The results in Table 8.3 show that the first PHRR is reduced from 516 kW/m^2 in the flax/PP to 263 kW/m^2 (50 % reduction), and second from 351 kW/m^2 to 240 kW/m^2 (30% reduction). Flax-FR(1%P)/PP-FR(1%P) also produced low THR of 78 MJ/m^2, which is the lowest value in

comparison to other flame retardant flax/PP samples. Flax-FR(1%P)/PP-FR(1%P) also shows significant improvement in char formation (18.4%) in comparison to the control (3.1%).

To further understand the effect of FR in individual components on reduction in flammability of the derived composites, the percent changes in important cone parameters of these FR flax/PP composites with respect to the control flax/PP composite are given in Table 8.4. It can be seen that with the use of flame retardant on either flax or PP components, the PHRRs of the derived composites can be reduced, and the reduction is similar in both systems. The THR is increased with FR on flax fabric only (Flax-FR(2%P)/PP). Whereas, to improve the TTI of the composites the flame retardant on flax fabric is effective as can be seen in Table 8.4 that flax/PP composites with only flame retardant on PP matrix show only small increase in TTI in comparison to the control, whereas the significant improvement was obtained with the flame retardant applied on to flax fabrics.

Table 8.4: Percent change in cone calorimetric results of FR flax/PP composites (all containing similar %P) compared to the control flax/PP at 35 kW/m^2

Sample	TTI	PHRR (1st peak)	THR	Yield
Flax/PP-FR(2%P)	+8%	-28%	-2%	+32%
Flax-FR(2%P)/PP	+206%	-26%	+16%	+529%
Flax-FR(1%P)/PP-FR(1%P)	+57%	-49%	-11%	+494%

Note: + and - indicates an increase and a reduction in the value w.r.t. the control sample, respectively

The difference in the effect of these two FRs on TTI of these composites could arise for two possible reasons. The first could be due to differences in the performance of the flame retardants used in each component (i.e. OP flame retardant on polymer matrix and GUP on flax fabric). OP flame retardant did not provide improvement on the TTI of the sample but only reduced the PHRR as can be seen from results in *Chapter 7,* whereas, the GUP flame retardant applied on to the flax component showed significant improvement in the TTI of the composites, (*Chapter 5)*. The second reason for the long delay of TTI in the Flax-FR(2%P)/PP sample could possibly be due to that during melt-pressing some of the flame retardant applied on the fabric may diffuse into the molten PP polymer, and help in reducing the combustibility of the PP. When FR is used in both components (sample Flax-FR(1%P)/PP-FR(1%P)) the reduction in PHRR and THR is much higher than the samples with FR in one component only. The TTI and char yield are also significantly higher than expected. This shows that by adding FR in each component, there is some type of FR (in particular GUP) diffusion to other component and some possible interaction of flame retardant(s) with both components. This observation needs further investigation and can be part of the future work.

On comparing the EHC of FR flax/PP composites prepared from different combinations of FR components, the results in Table 8.3 show that the use of flame retardant on either flax fabric or polymer matrix components provides only small improvement as can be seen from the EHC of

flax/PP composites which was only reduced from 23 MJ/kg in the control to 22 MJ/kg in all samples (i.e. Flax/PP-FR and Flax-FR/PP composites). Whereas, the use of FRs in both components shows better improvement in EHC as shown by the lowest EHC of 20 MJ/kg in Flax-FR(1%P)/PP-FR(1%P) in comparison to others.

In Figure 8.2, the relative overall fire performances of these FR flax/PP composites were also evaluated to compare the fire hazard of the composites by plotting the THR against the fire growth rate values, as calculated by dividing PHRR by TTI [2,3]. Fire safe materials should have low THR and fire growth rate value (PHRR/TTI) [2] and hence should be close to 0,0 co-ordinates of the 2-D graph. The results in Figure 8.2 show that with the use of flame retardant in PP matrix alone the fire safety of flax/PP was slightly improved as can be seen that although Flax/PP-FR composites show better fire growth rate results than the control, their THRs are marginally improved. In the case of the use of flame retardant on the flax component only, the Flax-FR(2%P)/PP shows much lower fire growth rate than the control, mainly due to the significant increase in TTI compared to the control (Table 8.3), but it produced higher THR during its combustion, hence resulting in the lower fire safety in Flax-FR(2%P)/PP in comparison to the control. A clear improvement in fire safety is only seen when use both flame retardant flax and PP matrix components to prepare flax/PP composites.

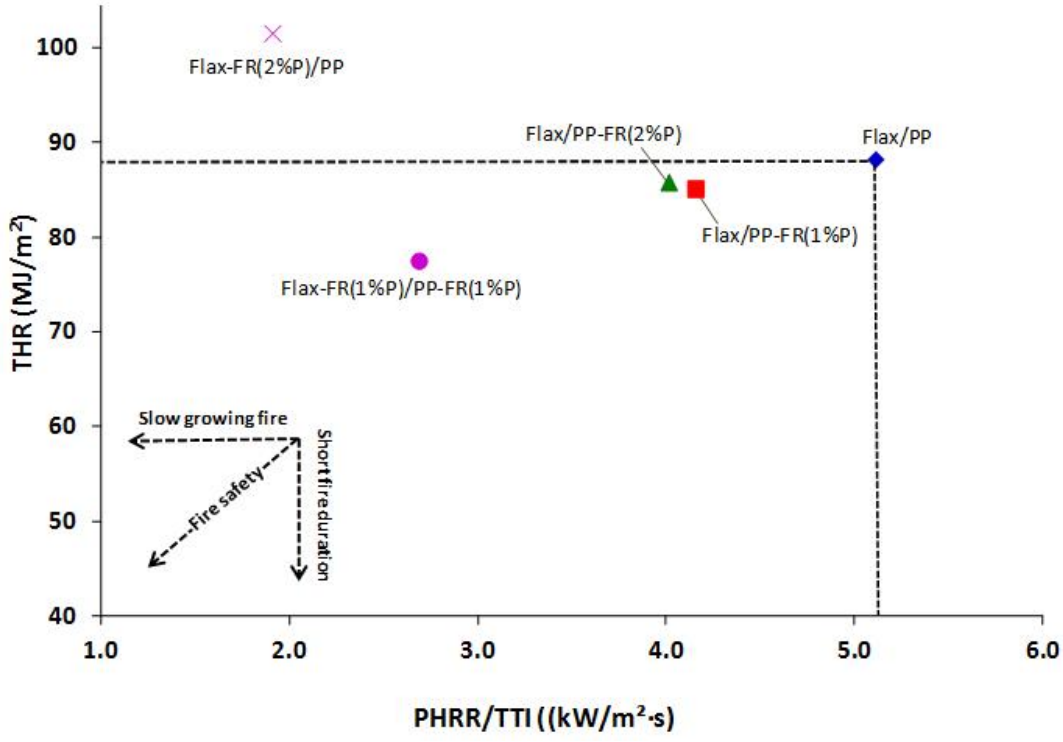

Figure 8.2: 2-D fire safety index of control and flame retardant flax/PP composites exposed to 35 kW/m^2 heat flux

From these results, it therefore can be concluded that with the use of flame retardant on either flax or PP matrix component alone the flammability of flax/PP composites is marginally improved, hence to obtain the maximum fire performance both components must be flame retarded.

Flax/PLA composites

In Table 8.5, the UL-94 results show that control flax/PLA composite failed the vertical rating test, and burned with rates of burning of 93.3 mm/min and 14.8 mm/min in vertical and horizontal orientations, respectively. With the use of a FR polymer matrix (i.e. PLA-FR), Flax/PLA-FR(1%P) shows a marginal improvement in flammability in comparison to the control as can be seen that Flax/PLA-FR(1%P) failed the vertical rating, and shows similar rates of burning when compared to the control flax/PLA, Table 8.5. With the increased FR content to 2 %P in PLA matrix, the flammability of the composites is slightly further reduced as shown by the lower vertical rate of burning of 72.2 mm/min, and no burning rate in horizontal orientation. In contrast, the use of flame retardant in flax fabric shows much reduction in flammability of flax/PLA composites as can be seen that Flax-FR(1.5%P)/PLA could pass V-0 rating, i.e. the sample did not ignite. A similar performance is also seen in Flax-FR(0.75%P)/PLA-FR(1%P), which also achieved V-0 rating.

Table 8.5: UL-94 results of control and flame retardant flax/PLA composites

Sample	Horizontal burning rate (mm/min)	Vertical burning rate (mm/min)	V-Rating
Flax/PLA	14.8 ±1.0	93.3 ±3.8	Failed
Flax/PLA-FR(1%P)	11.6 ±0.8	93.8 ±3.6	Failed
Flax/PLA-FR(2%P)	-*	72.2 ±4.9	Failed
Flax-FR(1.5%P)/PLA	-	-	V-0**
Flax-FR(0.75%P)/PLA-FR(1%P)	-	-	V-0**

* Flame went out before reaching timing mark

** Sample did not ignite

The cone calorimetric results of control and flame retardant flax/PLA composites at 35 kW/m^2 are presented in Figures 8.3 and Table 8.6.

Table 8.6: Cone calorimetric results of control and flame retardant flax/PLA composites at 35 kW/m^2

Sample	TTI	1st Peak		2nd Peak		THR	EHC	TSR	Char
	(s)	T_{PHRR} (s)	PHRR (kW/m^2)	T_{PHRR} (s)	PHRR (kW/m^2)	(MJ/m^2)	(MJ/kg)	(L)	(%)
Flax/PLA	52 ±6	65 ±4	347 ±24	143 ±13	294 ±17	71 ±3	14 ±1	10 ±1	4.4 ±0.8
Flax/PLA-FR(1%P)	54 ±3	68 ±6	329 ±13	103 ±8	266 ±16	54 ±2	13 ±1	225 ±61	6.7 ±1.6
Flax/PLA-FR(2%P)	54 ±2	65 ±1	316 ±7	118 ±3	239 ±10	50 ±5	12 ±1	221 ±34	7.6 ±1.5
Flax-FR(1.5%P)/PLA	76 ±3	91 ±6	274 ±14	200 ±16	188 ±5	54 ±6	11 ±1	25 ±15	18.5 ±0.6
Flax-FR(0.75%P)/PLA-FR(1%P)	68 ±4	83 ±5	270 ±9	153 ±5	187 ±9	47 ±2	11 ±1	45 ±36	18.0 ±0.8

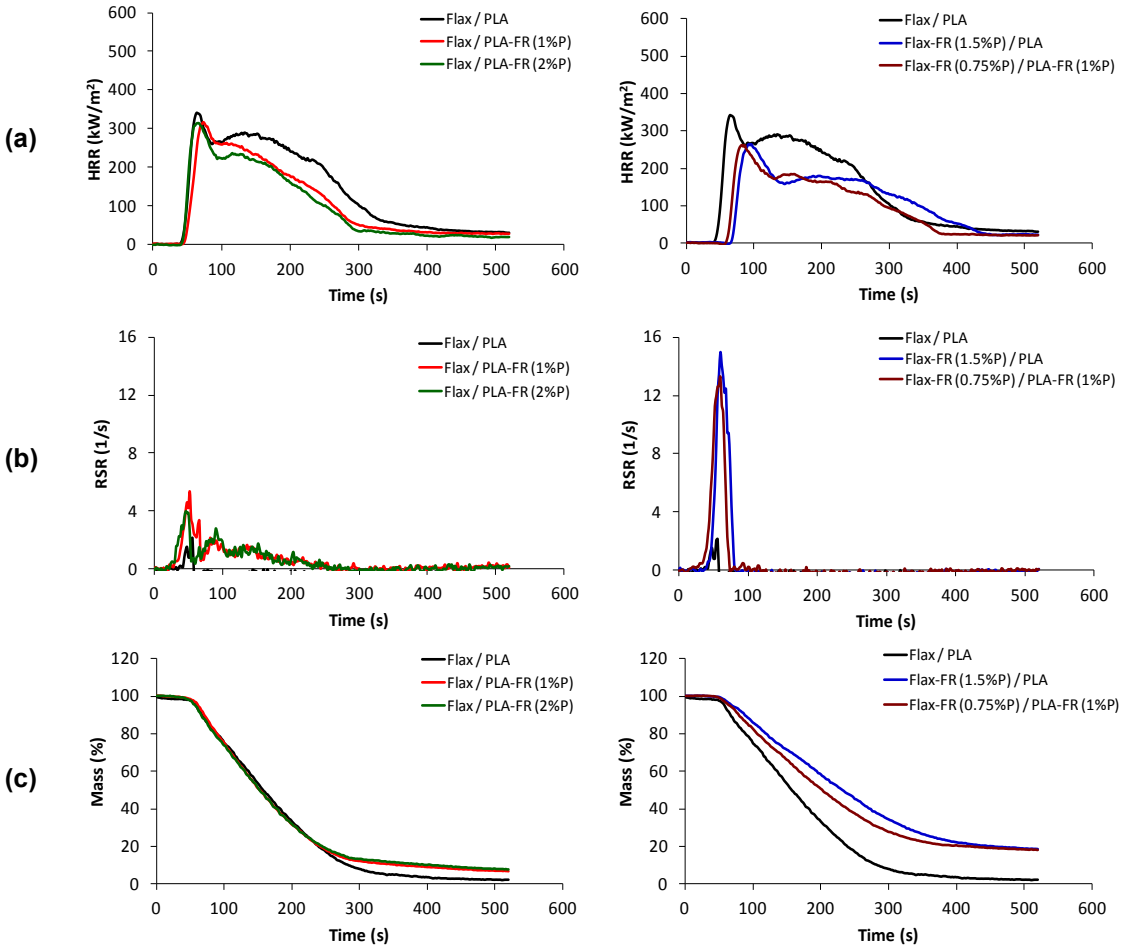

Figure 8.3: Cone calorimetric results of control and flame retardant flax/PLA composites at 35 kW/m^2: (a) HRR, (b) RSR, and (c) mass loss curves as a function of time

The results in Table 8.6 show that flax/PLA composites without any flame retardant ignited at 52 s, and burned with two PHRRs of 347 and 294 kW/m^2, producing 71 MJ/m^2 THR. Flax/PLA show small char formation (2.4%) after combustion. With the use of OP flame retardant on PLA matrix alone, a similar effect to that observed in flax/PP samples is seen, i.e. the use of only flame retardant (i.e. OP flame retardant) in PLA matrix does not show an effect on TTI, but decreases PHRRs of flax/PLA composites. Flax/PLA-FR(1%P) shows similar TTI (54 s) as in the control (52 s), and burned with slightly lower PHRRs of 329 and 266 kW/m^2. The HRR curves in Figure 8.3 also show that the use of PLA-FR component causes the Flax/PLA-FR(1%P) to burn for a shorter time than the control and even the reduction in PHRRs in Flax/PLA-FR(1%P) as compared to the control is not significant, it however produced a much lower THR (54 MJ/m^2) than the control (71 MJ/m^2). With the increase OP content on PLA component, there is no effect on the TTI of Flax/PLA-FR(2%P) in comparison to Flax/PLA-FR(1%P), but the PHRRs are reduced slightly further to 316 kW/m^2 for the first peak and 239 kW/m^2 for the second, resulting in a slightly lower THR in Flax/PLA-FR(2%P) (50 MJ/m^2) as compared to Flax/PLA-FR(1%P) (54 MJ/m^2). The use of the flame retardant flax component (i.e. flax treated with GUP) to prepare flax/PLA composites does show significant improvement in

TTI and reduction in PHRRs in Flax-FR(1.5%P)/PLA in comparison to the control, as can be seen that Flax-FR(1.5%P)/PLA show significantly higher TTI (76 s) than the control (52 s), and lower PHRRs of 274 and 188 kW/m^2. However, the HRR curves in Figure 8.3 show an effect similar to flax/PP samples that the use of flame retardant on flax component causes the Flax-FR(1.5%P)/PLA to burn for a longer time than the control, hence although Flax-FR(1.5%P)/PLA shows better reduction in PHRRs as compared to other Flax/PLA-FR samples, it produced a similar THR (54 MJ/m^2) as observed in the latter, Table 8.6. The use of flame retardants in both components, Flax-FR(0.75%P)/PLA-FR(1%P) shows relatively high TTI (68 s), lower PHRRs (270 and 187 kW/m^2), lower THR (47 MJ/m^2), lower smoke production (45 l) and higher char (18%) in comparison to samples with FR in one component only. This can be seen more clearly from Table 8.7 where percent changes in important cone parameters of these FR flax/PLA composites with respect to the control flax/PLA composite are presented.

Table 8.7: Percent change in cone calorimetric parameters of FR flax/PLA composites compared to the control flax/PLA at 35 kW/m^2

Sample	TTI	PHRR (1st peak)	THR	Yield
Flax/PLA-FR(1%P)	+10%	-5%	-24%	+52%
Flax/PLA-FR(2%P)	+10%	-9%	-30%	+73%
Flax-FR(1.5%P)/PLA	+46%	-21%	-24%	+420%
Flax-FR(0.75%P)/PLA-FR(1%P)	+31%	-22%	-34%	+310%

Note: + and - indicates an increase and a reduction in the value w.r.t. the control sample, respectively

The EHC results in Table 8.6 show that the use of flame retardants either on flax fabric, PLA matrix, or both components reduced the flammability of flax/PLA composites. On comparing the EHC of these flame retardant flax/PLA composites, Flax-FR(1.5%P)/PLA and Flax-FR(0.75%P)/PLA-FR(1%P) show the highest reduction in the EHC (11 MJ/m^2) in comparison to the control (14 MJ/m^2), followed by Flax/PLA-FR(2%P) and Flax/PLA-FR(1%P) with the EHC of 12 and 13 MJ/m^2, respectively. This also indicates that the use of flame retardant on flax component was more effective than using FR on PLA matrix.

The relative overall fire performance of these flame retardant flax/PLA composites in Figure 8.4 also shows similar trend as discussed above that Flax-FR(0.75%P)/PLA-FR(1%P) is safer than Flax-FR(1.5%P)/PLA followed by Flax/PLA-FR(2%P) and Flax/PLA-FR(1%P), respectively.

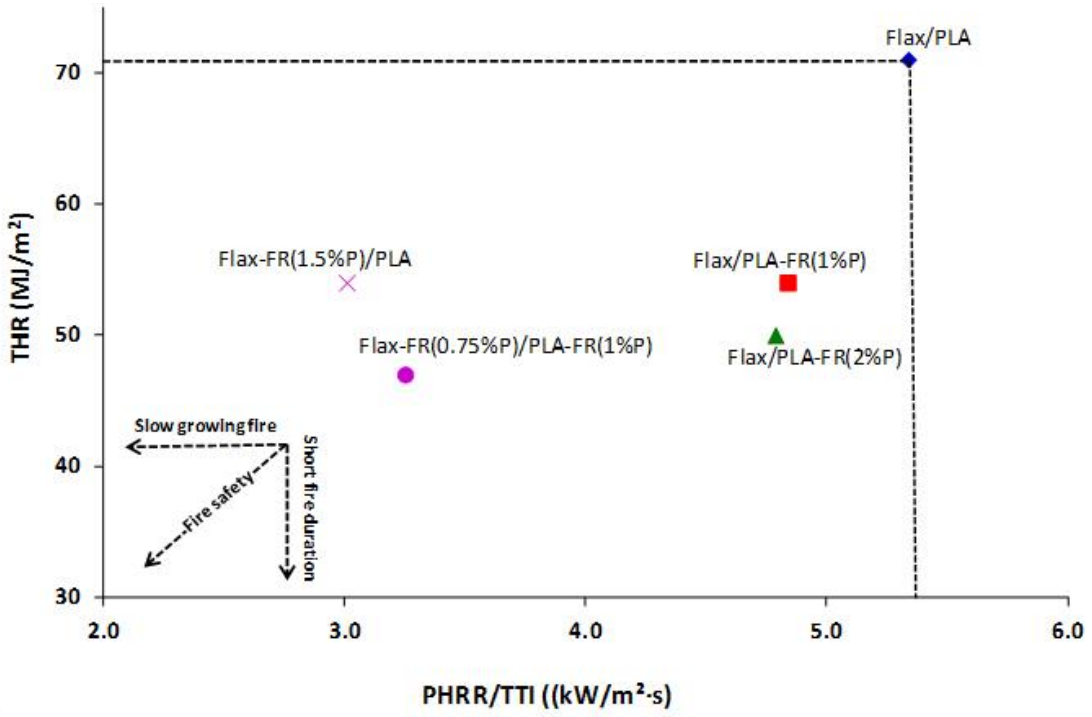

Figure 8.4: 2-D fire safety index of control and flame retardant flax/PLA composites exposed to 35 kW/m^2 heat flux

8.1.2 Mechanical performance of flame retardant flax/PP and flax/PLA composites

The mechanical properties of flax/PP and flax/PLA composites were evaluated in tensile and flexural mode in order to study for the effect of flame retardant components on the overall mechanical performance of the composites as shown in Table 8.8 and 8.9.

Table 8.8: Mechanical properties of control and flame retardant flax/PP composites

Sample	Tensile properties		Flexural properties	
	Modulus (GPa)	Strength (MPa)	Modulus (GPa)	Strength (MPa)
Flax/PP	7.7 ±0.3	94 ±2	9.2 ±0.2	54 ±1
Flax/PP-FR(1%P)	7.0 ±0.1 [-10%]	82 ±1 [-13%]	8.3 ±0.8 [-10%]	57 ±2 [+6%]
Flax/PP-FR(2%P)	6.9 ±0.5 [-10%]	79 ±2 [-16%]	7.4 ±0.6 [-20%]	52 ±9 [-4%]
Flax-FR(2%P)/PP	5.0 ±0.2 [-35%]	45 ±2 [-51%]	6.0 ±0.1 [-35%]	33 ±3 [-39%]
Flax-FR(1%P)/PP-FR(1%P)	6.0 ±0.4 [-22%]	56 ±5 [-40%]	7.8 ±0.5 [-15%]	47 ±3 [-13%]

Note: Fibre volume fractions in all flax/PP samples are ~ 40%, values in brackets are percent change of the properties with respect to the respective control samples

Flax/PP composites

In tensile mode, control flax/PP laminate shows 7.7 GPa tensile modulus and 94 MPa tensile strength. With the use of flame retardant PP matrix, the tensile properties of flax/PP are slightly decreased as can be seen that Flax/PP-FR(1%P) shows slightly lower tensile modulus (7.0 GPa, 10% reduction) and strength (82 MPa, 13% reduction) in comparison to the control, Table 8.8. With higher FR content in the matrix component, there is no further effect on the tensile properties of the composites as can be seen from the similar tensile properties of Flax/PP-

FR(2%P) and Flax/PP-FR(1%P). This is because the tensile properties of composites are fibre dependent [4], hence the change in polymer matrix causes only small changes in the tensile properties of the composites. Whereas, the results in Table 8.8 show that the use of GUP on flax fabrics causes significant reduction in tensile properties of flax/PP composites as can be seen from the lower tensile modulus (5.0 GPa, 35% reduction) and strength (45 MPa, 51% reduction) of Flax-FR(2%P)/PP in comparison to the control. This was as expected as the GUP treatment could decrease mechanical properties of flax fibre due to its acidity causing the hydrolysis of cellulose in flax fibres (discussed in details in *Chapter 5*), and also causes a significant reduction in fibre/matrix interfacial adhesion in the composites (discussed in *Chapter 6)*, which then results in poor load-transfer between fibre and matrix in composites [5]. This therefore leads to a significant reduction in tensile properties of Flax-FR(2%P)/PP in comparison to the control, Table 8.8. With the use of combination of flame retardant flax fabric and PP matrix components, the significant reduction in tensile properties of Flax-FR(1%P)/PP-FR(1%P) as compared to the control are also observed, but the effect is less severe than using flame retardant only in flax component (i.e. Flax-FR(2%P)/PP) as can be seen from % reduction values for both parameters in Table 8.8, which can be explained due to lower FR content on flax fabric in Flax-FR(1%P)/PP-FR(1%P). In flexural mode, the use of FR matrix component causes a small reduction in flexural modulus of flax/PP composites as can be seen that the use of PP-FR matrix slightly reduced the flexural modulus of flax/PP from 9.2 GPa in the control to 8.3GPa in Flax/PP-FR(1%P), and reduced further with higher FR content on PP matrix to 7.4 GPa in Flax-PP-FR(2%P). This arises because the flexural properties of composites are matrix dependent, so changes in properties of polymer matrix also show an effect on the flexural properties of the derived composites. With the use of flame retardant (i.e. GUP) on flax fabrics, the flexural properties of flax/PP composite were also reduced, and the effect is more severe than that observed in Flax/PP-FR composites as can be seen that Flax-FR(2%P)/PP show significantly lower flexural modulus (6.0 GPa) and strength (33 MPa) in comparison to the control, Table 8.8. This could be due to some of the flame retardant migrating to the matrix during melt pressing and hence, reducing the flexural performance of the composite, the performance being matrix dependent [4]. Moreover, the results in *Chapter 6* showed that the GUP flame retardant caused a significant reduction in fibre/matrix interfacial adhesion between flax and PP, which results in delamination and reduction in flexural properties of the composites. Hence, the high GUP content on flax fabrics (2% P), leads to a significant reduction in flexural properties of Flax-FR(2%P)/PP in comparison to the control, Table 8.8. The results in Table 8.8 show that with the use of the combination of flame retardant flax fabrics and PP components a reduction in flexural properties was also observed in Flax-FR(1%P)/PP-FR(1%P), but the reduction was lower (15%) than that observed in Flax-FR(2%P)/PP (35%), which could be due to the lower GUP content on flax component (i.e. 1% P) in the former.

Flax/PLA composites

In the case of flax/PLA composites, the tensile results in Table 8.9 show that the control flax/PLA has 8.3 GPa tensile modulus and 105 MPa tensile strength.

Table 8.9: Mechanical properties of control and flame retardant flax/PLA composites

Sample	Tensile properties		Flexural properties	
	Modulus (GPa)	Strength (MPa)	Modulus (GPa)	Strength (MPa)
Flax/PLA	8.3 ±0.1	105 ±3	10.5 ±0.2	121 ±11
Flax/PLA-FR(1%P)	8.3 ±0.3 [-]	116 ±3 [+10%]	9.9 ±1.1 [-6%]	115 ±22 [-5%]
Flax/PLA-FR(2%P)	8.4 ±0.4 [+1%]	113 ±7 [+8%]	9.6 ±0.1 [-9%]	115 ±15 [-5%]
Flax-FR(1.5%P)/PLA	7.1 ±0.3 [-14%]	84 ±3 [-20%]	9.2 ±0.1 [-12%]	102 ±8 [-16%]
Flax-FR(0.75%P)/PLA-FR(1%P)	7.8 ±0.5 [-6%]	110 ±9 [+5%]	10.0 ±0.4 [-5%]	113 ±14 [-7%]

Note: Fibre volume fractions in all flax/PLA samples are ~ 60%, values in brackets are percent change of the properties with respect to the respective control samples

The use of flame retardant only on PLA matrix component did not show an effect on tensile properties of flax/PLA as can be seen that both Flax/PLA-FR(1%P) and Flax/PLA-FR(2%P) show similar tensile modulus (~8.3 GPa) and tensile strength (~110 MPa) as observed in the control, Table 8.9. This was as expected due to tensile properties of composites being fibre dependent. Whereas, the results of flax/PLA composites incorporating FR treated flax fabric show that the use of flame retardant on the flax component alone causes reduction in tensile properties of flax/PLA, Flax-FR(1.5%P)/PLA shows lower tensile modulus (7.1 GPa, 14% reduction) and strength (84 MPa, 20% reduction) in comparison to the control, Table 8.9. This observation was similar to that in flax/PP samples, hence could be explained in similar manner that the addition of GUP on flax fabric causing reduction in mechanical properties of flax fibre, matrix and fibre/matrix interfacial adhesion, thereby resulting in the reduction in tensile properties of the composites. Flax-FR(0.75%P)/PLA-FR(1%P) also shows reduction in tensile properties as compared to the control, but the effect is less severe as can be seen the reduction in tensile modulus by about 6% in Flax-FR(0.75%P)/PLA-FR(1%P) as compared to the control, and there is no change observed in tensile strength of these composites. This is because in comparison to the Flax-FR(1.5%P)/PLA, the GUP content on flax fabric in Flax-FR(0.75%P)/PLA-FR(1%P) is lower, hence, there is less effect of GUP on the properties of the composites. The flexural properties of flame retardant flax/PLA composites in Table 8.9 show similar trend as observed in the flax/PP samples, i.e. with the use of flame retardant components flexural properties were reduced in all flame retardant flax/PLA samples as compared to the control. The use of PLA-FR matrix slightly decreased the flexural modulus of flax/PLA from 10.5 GPa to 9.9 GPa in Flax/PLA-FR(1%P) (6% reduction), and the flexural strength from 121 to 115 MPa (5% reduction). With the higher FR content (2% P), Flax/PLA-FR(2%P) shows further reduction in flexural modulus to 9.6 GPa (9% reduction compared to the control), but the flexural strength remained similar to that of Flax/PLA-FR(1%P). The use of FR only on the flax component shows higher reduction in flexural properties, as seen from the lower flexural modulus (9.2 GPa, 12% reduction) and strength (102 MPa, 16% reduction) in Flax-

FR(1.5%P)/PLA. With the use of FR on both components, Flax-FR(0.75%P)/PLA-FR(1%P) shows lower flexural properties than the control with 10 GPa flexural modulus (5% reduction) and 113 MPa flexural strength (7% reduction). These values are similar to that observed in Flax/PLA-FR(1%P), i.e. ~ 5% reduction in both flexural modulus and strength as compared to the control. This could be due to the FR content on flax component is comparatively low, hence the effect from GUP was minimum and the reduction in flexural properties of the composites was mainly from the PLA-FR matrix (i.e. PLA-FR(1%P)).

In conclusion, to obtain the high performance flame retardant thermoplastic natural fibre composites with minimal reduction in mechanical performance (flame retardants are required on both flax and polymer components

8.2 Flame retardant flax/furan composites

To study the effect of different FR components on fire and mechanical performances of flax/furan composites, a number of composite laminates with fibre/matrix ratio 50/50 by weight from different combinations of FR treated flax fabrics and flame retardant furan resin as listed in Table 8.10 were produced by using a prepreging technique. Details of the prepreging procedure are described in *Section 3.2.4*, *Chapter 3*. The FR treated flax fabric was prepared by treating flax with GUP to obtain 1.5% P content on the fabric. Ammonium polyphosphate (APP) and melamine polyphosphate (MPP) were chosen to flame retard the furan resin matrix at specific P contents as given in Table 8.10. These selected concentrations were chosen based on the results obtained in *Chapter 7*.

Table 8.10: Sample preparation matrix of control and flame retardant flax/furan composites

Sample	Reinforcement	Resin	P content (%)
Flax/Furan	Flax	Furan	-
Flax/ Furan+APP(3.0%P)	Flax	Furan+APP(3.0%P)	1.5
Flax/ Furan+APP(6.0%P)	Flax	Furan+APP(6.0%P)	3.0
Flax/ Furan+MPP(2.6%P)	Flax	Furan+MPP(2.6%P)	0.65
Flax-FR(1.5%P)/ Furan+APP(3.0%P)	Flax+GUP (1.5%P)	Furan+APP(3.0%P)	2.25
Flax-FR(1.5%P)/ Furan+MPP(2.6%P)	Flax+GUP (1.5%P)	Furan+MPP(2.6%P)	1.4

Note: GUP = guanylurea methylphosphonate, APP = ammonium polyphosphate, MPP = melamine polyphosphate

8.2.1 Fire performance of flame retardant flax/furan composites

The flammability of flax/furan composites prepared from different combination as listed above was evaluated by using UL-94 and cone calorimetry (50 kW/m^2) techniques. The UL-94 results showed that all composites including control flax/furan could pass V-0 rating as the samples did not ignite, hence the difference in FR performance of different FR components on the flammability of flax/furan in this study is mainly discussed in terms of cone calorimetric results. The cone calorimetric results at 50 kW/m^2 external heat flux of control and flame retardant

flax/furan composites are presented in Figure 8.5 and reported in Table 8.11. The results in Table 8.11 show that control flax/furan composite ignited at 98 s, and burned with two peaks of HRR similar to that observed in flax/PP and flax/PLA composites. Flax/furan shows 364 kW/m^2 in the first peak and 441 kW/m^2 in the second at 112 s and 154 s, respectively. Flax/Furan produced 53 MJ/m^2 THR and 30.3% charred residue.

Table 8.11: Cone calorimetric results of control and flame retardant flax/furan composites at 50 kW/m^2

Sample	TTI	1st Peak		2nd Peak		THR	EHC	TSR	Char
	(s)	T_{PHRR} (s)	PHRR (kW/m^2)	T_{PHRR} (s)	PHRR (kW/m^2)	(MJ/m^2)	(MJ/kg)	(L)	(%)
Flax/Furan	98±5	112±1	364±33	154±6	441±33	53±1	10±1	173±26	30.3 ±0.1
Flax/Furan+APP(3.0%P)	206±1	221±7	173±9	-	-	15±2	3±1	48±1	43.3 ±0.7
Flax/Furan+APP(6.0%P)	285±4	301±1	36±2	-	-	2±1	1±1	22±23	48.3 ±0.9
Flax/Furan+MPP(2.6%P)	208±1	233±7	257±5	-	-	20±3	4±1	57±10	38.9 ±1.0
Flax-FR(1.5%P)/Furan+APP(3.0%P)	321±7	343±13	58±5	-	-	7±1	2±1	24±13	42.3 ±0.9
Flax-FR(1.5%P)/Furan+MPP(2.6%P)	252±6	272±8	87±4	-	-	7±1	2±1	20±5	44.6 ±0.2

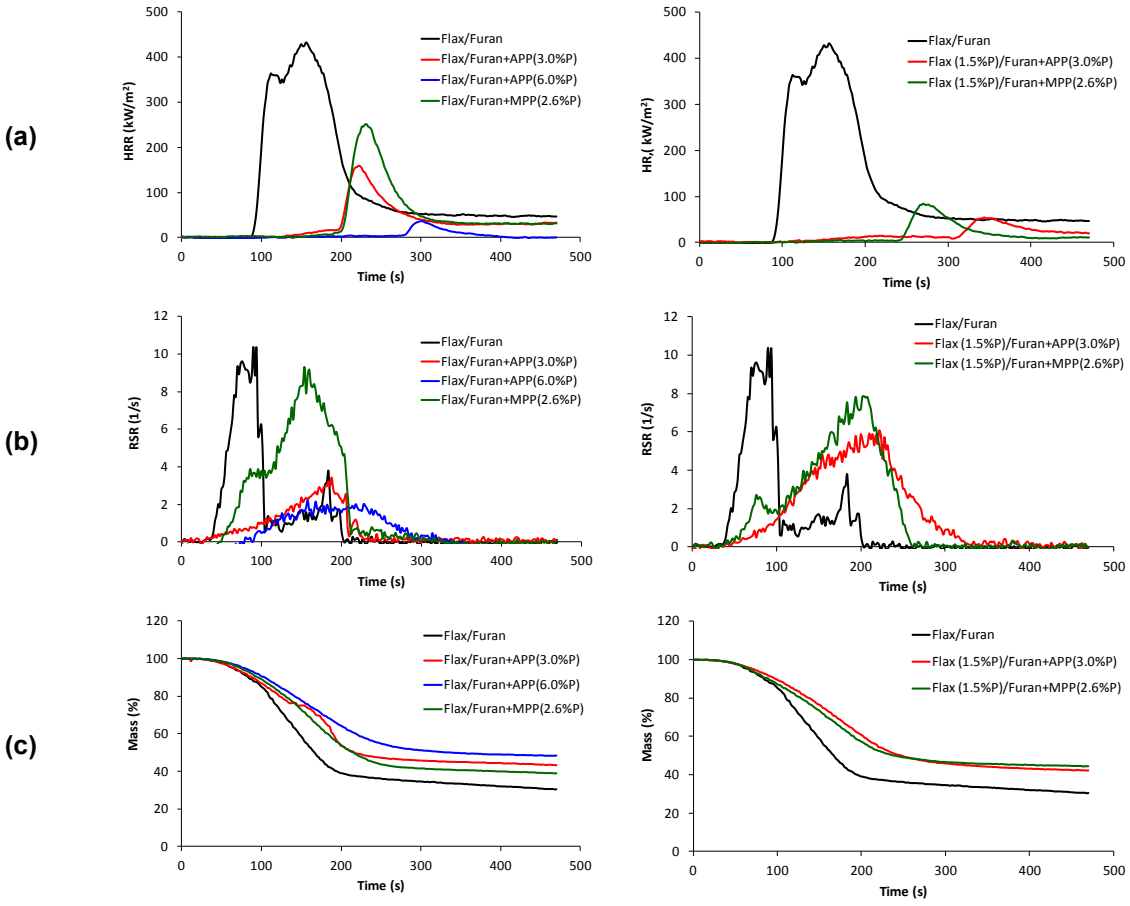

Figure 8.5: Cone calorimetric results of control and flame retardant flax/furan composites at 50 kW/m^2: (a) HRR, (b) RSR, and (c) mass loss curves as a function of time

With the use of flame retardant furan resin matrix, the flammability of flax/furan composites was reduced in all samples, the efficiency in reducing the flammability however varied depending on the type of flame retardant used in furan resin matrices. With APP at 3.0% P content, the results show that the Furan+APP(3.0%P) matrix significantly improved the TTI of flax/furan composite from 98 s to 206 s, and changed the burning behaviour of flax/furan composite from two peaks of HRR to single peak with much lower intensity (173 kW/m^2) as shown in Figure 8.5. The change in burning behaviour could be explained by the improvement in char formation of Flax/Furan+APP(3.0%P) (43.3%) as compared to the control (30.3%). The char formation could enhance the thermal barrier properties of the char formed on the surface of the composite to protect the underlying material, which in this case is a dominant factor, as can be seen that it could completely protect the underlying material from the heat and flaming zone, hence resulting in the change of burning behaviour of flax/furan laminate from double PHHRs to a single PHRR. This effect is also seen in all flame retardant flax/furan samples, Figure 8.5. With increase of the APP content to 6.0% P, the fire performance of flax/furan is significantly improved further as can be seen that Flax/Furan+APP(6.0%P) ignited at 285 s, and burned with a very low PHRR of 36 kW/m^2, producing an almost negligible THR of 2 MJ/m^2 as compared to the control (53 MJ/m^2 THR). The use of MPP flame retardant on the furan resin matrix component also reduced the flammability of flax/furan composites, but it was less effective than APP as can be seen such that Flax/Furan+MPP(2.6%P) shows TTI of 208 s, and a single PHRR with 257 kW/m^2 intensity at 233 s. Flax/Furan+MPP(2.6%P) produced slightly higher THR (20 MJ/m^2) as compared with Flax/Furan+APP composites. These results were as expected as the results in *Chapter 7* show that APP was more effective than MPP when flame retarding furan resin, hence the same effect is also expected to be seen in the derived composites. When flame retardant is used both on flax and furan resin components, the results show that the flammability of flax/furan composites was significantly reduced, Table 8.11. Flax-FR(1.5%P)/ Furan+APP(3.0%P) shows significant increase in TTI (321 s) as compared to the control (98 s), and burned with a low intensity single PHRR of 58 kW/m^2, producing 7 MJ/m^2 THR. In comparison to its respective flame retardant sample without flame retardant on flax component (Flax/Furan+APP(3.0%P)), these show that the additional flame retardant (i.e. GUP) on flax component could improve the flammability of flax/furan further as shown by higher TTI; lower PHRR and THR in Flax-FR(1.5%P)/Furan+APP(3.0%P). A similar trend is observed in Flax-FR(1.5%P)/Furan+MPP(2.6%P) as the additional flame retardant on flax reduced the flammability of Flax/Furan+MPP(2.6%P) further as can be seen that Flax-FR(1.5%P)/ Furan+MPP(2.6%P) ignited at longer time than Flax/Furan+MPP(2.6%P) at 252 s, and burned with lower PHRR of 87 kW/m^2, producing 7 MJ/m^2 THR.

The EHC results in Table 8.11 show that with the use of flame retardant components the flammability of flax/furan composites was significantly reduced as can be seen by the large reduction in EHC in all flame retardant flax/furan composites as compared to the control (10 MJ/kg). On comparing the performance of the flame retardant components used in the composites, the composite from Furan+APP(6.0%P) matrix shows the best performance,

Flax/Furan+APP(6.0%P) shows the lowest EHC value (1MJ/kg) as compared to others, followed by Flax-FR(1.5%P)/Furan+APP(3.0%P) and Flax-FR(1.5%P)/Furan+MPP(2.6%P) with 2 MJ/kg EHC, Flax/Furan+APP(3.0%P) (3 MJ/kg), and Flax/Furan+MPP(2.6%P) (4 MJ/kg), respectively.

In Figure 8.6, the relative overall fire performance of these composites also show the same trend as observed in EHC results where Flax/Furan+APP(6.0%P) is much safer than others, followed by Flax-FR(1.5%P)/Furan+APP(3.0%P), Flax-FR(1.5%P)/Furan+MPP(2.6%P), Flax/Furan+APP(3.0%P) and Flax/Furan+MPP(2.6%P), respectively.

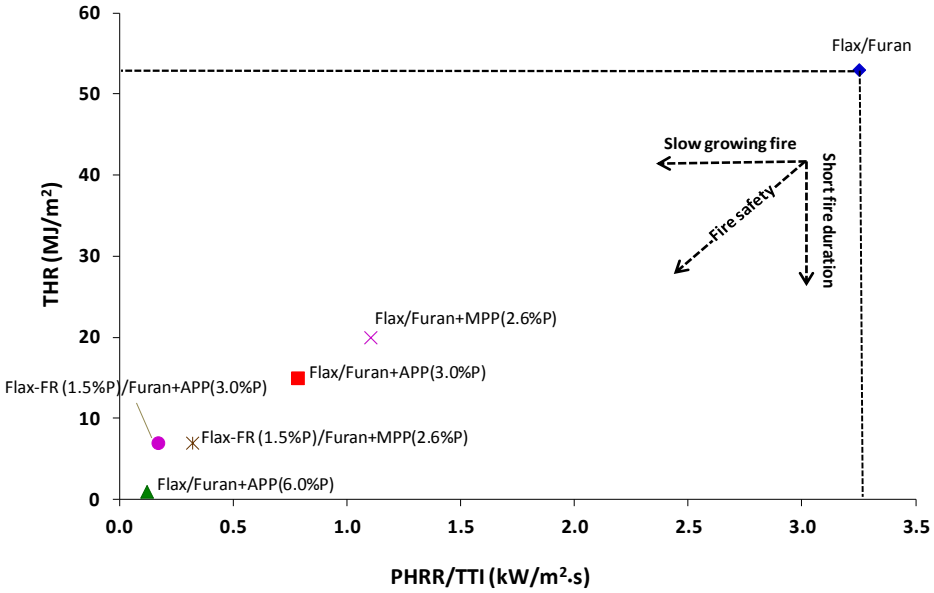

Figure 8.6: *2-D fire safety index of control and flame retardant flax/furan composites exposed to 50 kW/m^2 heat flux*

8.2.2 Mechanical performance of flame retardant flax/furan composites

The mechanical properties of control and flame retardant flax/furan composites in tensile and flexural modes are reported in Table 8.12.

Table 8.12: Mechanical properties of flame retardant flax/furan composites

Sample	Tensile properties		Flexural properties	
	Modulus (GPa)	Strength (MPa)	Modulus (GPa)	Strength (MPa)
Flax/Furan	6.3 ±0.1	67 ±2	9.4 ±0.2	91 ±5
Flax/Furan+APP(3.0%P)	6.0 ±0.2 [-5%]	50 ±1 [-25%]	8.6 ±0.2 [-9%]	82 ±13 [-10%]
Flax/Furan+APP(6.0%P)	6.0 ±0.4 [-5%]	47 ±1 [-30%]	8.5 ±0.2 [-10%]	81 ±11 [-11%]
Flax/Furan+MPP(2.6%P)	6.1 ±0.1 [-3%]	54 ±2 [-15%]	8.7 ±0.1 [-7%]	94 ±4 [+3%]
Flax-FR(1.5%P)/ Furan+APP(3.0%P)	4.3 ±0.6 [-32%]	44 ±1 [-35%]	4.8 ±0.1 [-49%]	60 ±7 [-34%]
Flax-FR(1.5%P)/ Furan+MPP(2.6%P)	4.5 ±0.2 [-29%]	39 ±2 [-42%]	5.5 ±0.1 [-41%]	61 ±4 [-33%]

Note: Fibre volume fractions in all flax/furan samples are ~48%, values in brackets are percent change of the properties with respect to the respective control samples

In tensile mode, flax/furan composite shows 6.3 GPa modulus and 67 MPa strength. The use of flame retardant on furan resin matrix (Furan-FR), the tensile properties of flax/furan were marginally affected as can be seen that all Flax/Furan-FR composites show similar tensile modulus (~6.0 GPa) as in the control, and only a small reduction is observed in their tensile strength (~50 MPa) as compared to the control. This was as expected as tensile properties are fibre dependent, hence the effect from matrix component is minimal. With the use of additional flame retardant on flax fabric (Flax-FR) in Flax/Furan+APP(3.0%P), the results show that the tensile modulus was reduced from 6.0 GPa in Flax/Furan+APP(3.0%P) to 4.3 GPa in Flax-FR(1.5%P)/Furan+APP(3.0%P), and the tensile strength was reduced from 50 MPa to 44 MPa. A similar trend is also observed in Flax-FR(1.5%P)/Furan+MPP(2.6%P) as the use of Flax-FR component reduced the tensile modulus of Flax/Furan+MPP(2.6%P) from 6.1 GPa to 4.5 GPa, and tensile strength from 54 MPa to 39 MPa. This indicates a negative effect of applying flame retardant (i.e. GUP) on flax component as it causes a reduction in tensile properties of flax/furan composites, which is similar effect as observed in flax/PP and flax/PLA composites. In flexural mode, flax/furan composite shows 9.4 GPa flexural modulus and 91 MPa strength. The results in Table 8.12 show that the use of FR furan resin matrix decreased the flexural properties of flax/furan composites, and there is no difference between results of composites from different flame retardants on the furan resin matrix. In comparison to the control, the reduction in these Flax/Furan-FR composites is however not significant as the flexural modulus of flax/furan is 9.4 GPa, which is reduced to ~8.5 GPa, and strength from 91 MPa to ~80 MPa. As flexural properties of composites are matrix dependent, this indicates that the use of flame retardant on furan component has marginal effects on the mechanical properties of furan resin. With the use of flame retardant flax fabric, the reduction in flexural properties of the composites is greater (i.e. 49% in flexural modulus in Flax-FR(1.5%P)/Furan+APP(3.0%P), and 41% in Flax-FR(1.5%P)/Furan+MPP(2.6%P), Table 8.12. This observation is similar to that observed for the flexural properties of flax/PP and flax/PLA composites containing flame retardant flax component.

To conclude, with addition of flame retardant, APP at 6.0% P content in the furan resin, the fire performance of flax/furan composites can be significantly enhanced without detrimental effect on mechanical properties. And there is no need of an additional flame retardant flax component in this case.

8.3 Conclusions

This study has shown that to obtain high performance flame retardant flax/PP composites both flax and PP components need to be flame retarded. The Flax-FR(1%P)/PP-FR(1%P) composite showed significant improvement in flammability with marginal effect on the mechanical properties. Similar results are also seen in flax/PLA samples as the highest fire and mechanical performance was observed from the composite prepared from the use of flame retardant on both flax and PLA component (i.e. Flax-FR(0.75%P)/PLA-FR(1%P)). Whereas, for flax/furan

composites, to obtain the maximum reduction in flammability and relatively high mechanical properties, the use of flame retardant in the furan resin matrix is sufficient. The inclusion of APP component at 6.0% P content in Flax/Furan+APP(6.0%P) achieved lowest THR and EHC in cone calorimetry; and relatively high mechanical properties as compared to other flame retardant flax/furan samples.

In figure 8.7 overall fire safety performances (evaluated from the cone calorimetric results) of all samples are summarised. It can also be seen that there is a correlation between the UL-94 rating and relative overall fire performance, all safer materials achieved V-0 rating in UL-94 test. It can be also estimated those natural fibre composites with THR lower than ~60 MJ/m^2 and fire growth rate lower than ~3.5 kW/m^2·s, will pass UL-94 test.

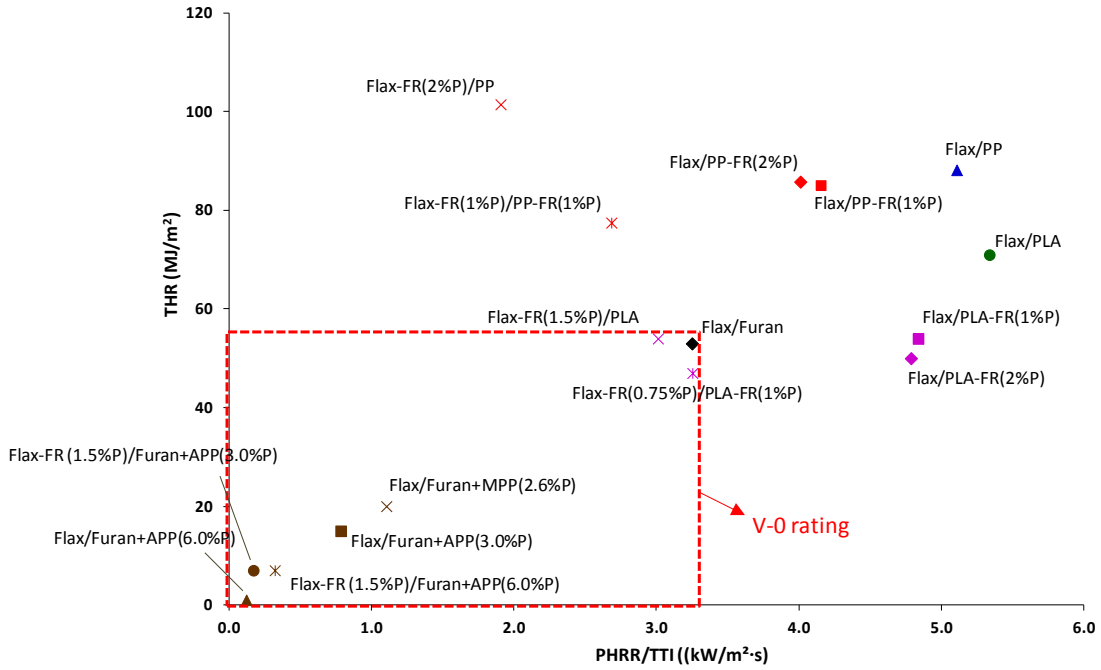

Figure 8.7: *2-D fire safety index of control and flame retardant natural fibre composites: flax/PP and flax/PLA exposed to 35 kW/m^2 heat flux, and flax/furan exposed to 50 kW/m^2 heat flux*

8.4 References

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Chapter 9: Conclusions

The aim of this project was to develop high performance flame retardant natural fibre reinforced composites by using FR treated fibres and/or polymer matrices with FR treatment. To achieve this, firstly the flammability of different natural fibres and bio/synthetic polymers was studied by using limiting oxygen index (LOI), UL-94 and cone calorimetry to identify suitable components for producing FR natural fibre composites (*Chapter 4*). The flammability results of different natural fibres showed that wool and flax fibres are less flammable than others. However, since in composite applications, the mechanical performance of a reinforcing fibre is the most important criterion for its selection, wool which has relatively low mechanical properties was discarded. Only flax fibre was selected for developing high performance natural fibre composites, mainly due to commercial interest in this fibre, its good mechanical properties and satisfactory fire performance, as compared to other natural fibres. For polymer matrix, the flammability results of different synthetic and bio based thermoplastic and thermoset polymers in *Chapter 4* showed that the biopolymers of polylactic acid (PLA) and poly(furfuryl alcohol) (furan resin) were less flammable in their respective groups of polymers. Also due to the environmentally friendly properties as being bio derived materials, PLA and furan resin were chosen as thermoplastic and thermoset polymer matrices, respectively, for natural fibre composites. In the group of thermoplastic matrices, polypropylene (PP) which showed high flammability was also selected for further study as commercially PP is the most popular polymer matrix currently used for natural fibre composites.

Various strategies to develop high performance flame retardant (FR) natural fibre composites from these identified materials were then adopted. These include (i) development of FR composites from FR treated flax/PP and flax/PLA commingled woven fabrics (*Chapter 5*), (ii) surface modification of flax/PP and flax/PLA fabrics for improving fibre-matrix adhesion in FR composites (*Chapter 6*), (iii) development of FR bio/synthetic polymer matrix (*Chapter 7*), and (iv) identification of a suitable FR strategy involving synergistic combinations of different FR components for producing high performance FR natural fibre composites (*Chapter 8*). The fire performance of the developed flame retardant natural fibre composites was evaluated by using UL-94 and cone calorimetry, while the mechanical performance was studied by tensile and flexural testing. The main conclusions drawn from the flammability and mechanical results of these composites are presented in the following sections.

9.1 Flame retardant composites from FR treated flax/PP and flax/PLA fabrics (*Chapter 5*)

By using commingled woven flax/PP and flax/PLA fabrics to prepare natural fibre composites, it was established that the best way to render these flame retardant was to treat fabrics with an aqueous FR solution by using a conventional pad-dry technique, as commonly used in textile applications. Usually for textile finishes, fabrics are scoured prior to other treatments in order to

remove impurities present in the fibres, resulting in an improvement in absorption of dyes and other finishes into the fibre. However not much is known about the effect of scouring on physical, mechanical and flammability properties of the composites, hence the fire and mechanical performances of FR flax/PP and flax/PLA from scoured fabrics were evaluated by using ammonium phosphate as a model flame retardant. The results in *Section 5.1* (*Chapter 5*) showed that the scouring process helped in increasing the FR uptake ability of flax/PP and flax/PLA fabrics, hence increasing the FR content on the laminates prepared from these fabrics. The fire performance of FR flax/PP and flax/PLA composites from scoured fabrics however was not improved as expected from the increased FR content. PHRRs, THR and EHC from cone calorimetric results increased in the composites from scoured fabrics as compared to the non-scoured ones, which could be explained by the removal of lignin and pectin, which have higher thermal stability than the cellulosic structure, on flax fibres during scouring. Scouring however helped in increasing the mechanical properties, which was due to a change in the morphology of flax fibres with production of rough surfaces, leading to improvement in fibre/matrix interfacial bonding by increasing additional sites of mechanical interlocking between fibre and matrix. The increase in mechanical properties through the scouring process though is minimal. Since with scouring, the flame retardancy of the laminates is slightly reduced and the enhancement in mechanical properties is also marginal, it was concluded that there is no benefit of the fabric pre-treatment (scouring process) prior to flame retardant treatment of the fabrics for producing FR flax/PP and flax/PLA composites.

To identify an effective flame retardant for the composites, the fabrics were treated with four different water soluble FRs (ammonium sulfamate, ammonium bromide, guanidine dihydrogen phosphate, and guanylurea methylphosphonate) without pre-treating prior to laminate preparation (*Section 5.2*). Out of these FRs, the flammability results of the flame retardant flax/PP and flax/PLA composites showed that guanylurea methylphosphonate (GUP) was the most effective flame retardant in both composite systems, as at 10 wt-% GUP content on the laminates both GUP-Flax/PP and GUP-Flax/PLA could pass V-0 rating in UL-94 test. The mechanical results however showed that GUP caused a decrease in mechanical properties of the composites, particularly tensile properties. This was due to the acidity of GUP solution causing damage to the flax fibres, resulting in reduction in mechanical properties of the derived composites. The formulation of GUP flame retardant was therefore further optimised. On varying the GUP content on flax/PP and flax/PLA composites in *Section 5.3*, the results showed that to obtain maximum flammability improvement (i.e. V-0 rating) with minimum effect on mechanical properties the GUP content of 0.9 and 0.6% P contents were required on flax/PP and flax/PLA, respectively. To minimise the effect of the flame retardants on mechanical properties, the effect of pH on the properties was also studied. The pH of the flame retardant solution was varied by adding sodium acetate (NaOAc) to it. The mechanical results in *Section 5.4* show that the reduction in the acidity of the GUP solution slightly improved mechanical properties of GUP-Flax/PP, but caused reduction in GUP-Flax/PLA. The reduction in mechanical properties in GUP-Flax/PLA can be explained in that NaOAc may cause hydrolysis

of the PLA matrix. The addition of NaOAc increased the flammability of GUP-Flax/PP and GUP-Flax/PLA composites, especially causing the failure in UL-94, while at pH 3.2 it had passed (V-0). Hence, from all these results it could be concluded that in oder to obtain high fire performance flame retardant flax/PP and flax/PLA composites, the optimised FR treatment conditions were to treat flax/PP and flax/PLA fabrics with GUP solution to obtain 0.9 and 0.6% P contents on flax/PP and flax/PLA, respectively, without reducing the acidity of GUP solution with NaOAc.

9.2 Surface modification for improving fibre/matrix interfacial adhesion of FR flax/PP and flax/PLA composites (*Chapter 6*)

Different surface modification treatments (i.e. silane treatment, atmospheric argon-plasma treatment, and the combination of both) on flame retardant flax/PP and flax/PLA woven fabrics (i.e. GUP treated fabrics with 0.9 and 0.6% P contents on flax/PP and flax/PLA, respectively) prior to laminate preparation have been attempted to improve fibre/matrix interfacial adhesion in the derived composites. In the first instance, flax/PP and flax/PLA fabrics, without any FR treatment, were treated with silane or plasma by using different conditions in order to identify an optimised condition for each type of treatment from which 3 wt-% silane solution and 150 kW plasma intensity were identified for silane and plasma treatment, respectively. With these identified conditions, the FR flax/PP and flax/PLA laminates were then prepared from FR treated flax/PP and flax/PLA fabrics treated with either silane, plasma, or the combination of both, and characterised for fibre/matrix interfacial adhesion of the derived composites by using peeling and flexural testing. The results showed that the fibre/matrix interfacial adhesion of FR treated flax/PP composites was improved with all surface modification treatments, and the best results were obtained with the combination of silane and plasma treatment. The results in FR treated flax/PLA composites showed that silane had no effect on the fibre/matrix interfacial adhesion of FR treated flax/PLA, hence to obtain the maximum improvement in fibre/matrix interfacial adhesion in FR treated flax/PLA laminates only plasma treatment is required.

9.3 Development of polymer matrices (*Chapter 7*)

Since one of the objectives was to develop flame retardant natural fibre composites by using a flame retardant polymer matrix component, the polymers identified in *Chapter 4* (i.e. thermoplastic: polylactic acid (PLA) and polypropylene (PP), and thermoset: poly(furfuryl alcohol) (furan resin)) were flame retarded by adding different phosphorus (P) based flame retardants to them. In thermoplastics, flame retardants were incorporated by melt-blending in a twin screw compounder, while in the thermoset they were mixed with the resin by mechanical stirring. The flammability of these flame retardant polymers were then characterised by using LOI, UL-94 and cone calorimetry to identify the most effective FR formulation for each polymer system. For developing flame retardant thermoplastic matrices with an aim to eventually extrude into fibres to be used as part of flax/PLA and flax/PP commingled fabrics, three different P based flame retardants (organic nitrogen-phosphorus compound (NP), organic phosphorus

compound (OP) and zinc phosphinate (ZP)) were added to PLA by melt-blending, and investigated for their flammability and fibre extrusion processability. The flammability results showed that NP and OP flame retardants were the most effective as with only 1% P level in each FR polymer, V-0 rating could be achieved. However, only PLA+OP samples could be extruded into filaments, and the maximum OP content that could be processed was 2% P level (8.4% solid FR content). Based on these results, OP flame retardant with the good processability was used for producing FR-PP fibres. The results showed that OP flame retardant also improved the flame retardance of PP, but was less effective than in PLA as with 1 and 2% P content only V-2 rating could be achieved in the UL-94 test. The fibre extrusion of PP+OP samples was also explored to identify the maximum OP content in PP that could be processed into filaments where the results showed that OP flame retardant at 1% P level (4.2% solid content) was the maximum to be processable. From all these results, the optimised FR formulations for producing flame retardant PLA and PP fibres to be used for natural fibre composites were therefore identified as PLA+OP(2%P) and PP+OP(1%P), respectively.

To develop flame retardant furan resin, different P based flame retardants, namely RDP (resorcinol bis(diphenyl phosphate)), BAPP (bisphenol A bis(diphenyl phosphate)), DOPO (9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide), APP (ammonium polyphosphate) and MPP (melamine polyphosphate) were introduced into the furan resin. Of these FRs, APP and MPP were seen to be the most effective in comparison as these significantly increased the LOI value of furan resin, and reduced the PHRR, THR and EHC of the resin by more than 50% in cone calorimetric results. Therefore, furan resins containing APP and MPP were chosen for producing flame retardant natural fibre reinforced thermoset composites.

9.4 Flame retardant natural fibre composites from different combination of FR components (*Chapter 8*)

From the identified flame retardant components (i.e. GUP treated flax and FR polymer matrices as developed in *Chapter 5* and *7*, respectively), a number of composites were prepared by using different combinations of these components, and their flammability and mechanical properties were evaluated in order to identify the most effective method of preparing high performance flame retardant natural fibre composites. The combination included: (i) control flax and FR polymer matrix (Flax/Polym-FR), (ii) FR treated flax and control polymer (Flax-FR/Polym), and (iii) FR treated flax and FR polymer (Flax-FR/Polym-FR). Comparison of the flammability and mechanical properties of flax/PP composites prepared from different combinations of FR components showed that to obtain the high performance flame retardant flax/PP composites both flax and PP components needed to be flame retarded. This provided significant reduction in flammability with marginal effect on the mechanical properties as compared to the untreated flax/PP composites. Similar results were also seen in flax/PLA samples as the best fire and mechanical performance was observed from the composite prepared from the use of flame retardant on both flax and PLA components.

On the other hand, the results of flax/furan composites showed that to obtain the maximum improvement in fire performance with relatively high mechanical properties in flame retardant flax/furan composites, use of APP flame retardant at 6.0% P content in the furan resin matrix was required. The derived composite showed lowest THR and EHC in cone calorimetry; and relatively high mechanical properties in comparison to other flame retardant flax/furan samples.

9.5 Suggestions for future work

Since this PhD project was commercially driven an in-depth study of some interesting observations could not be performed which could be the focus of the future work. These include:

(i) On treating Flax/PP and flax/PLA commingled fabrics with different FR solutions, the mechanical properties of the derived composites decreased at a particular FR concentration. It will be interesting to further evaluate the reason of this behaviour so that alternative solution or FR can be identified.

(ii) The mechanism of action of FRs both on flax fabric and polymer needs further investigation.

(iii) It is also important to investigate that how much FR transfers from one component to another during melt pressing while preparing composite laminates. This is particularly important when FRs are used on both flax fabric and in the polymer matrix, as this could develop a better understanding of how these two FRs interact with each component, and whether there is any synergistic or antagonistic interaction between two types of flame retardants.

The purpose of this PhD project was to develop high performance flame retardant natural fibre composites, by incorporating flame retardants into composite's components. However, the surface coating with flame retardant chemicals is an alternative solution to render these natural fibre composites flame retardant. A flame retardant coating layer applied on surfaces of composites could protect the composites from the heat source during burning, hence slowing down or stopping the combustion process. To achieve this, several coating strategies could be attempted such as an intumescent coating, a flame retardant coating (e.g. halogenated, phosphorus based flame retardant chemicals dispersed in a binder), and a silica coating, applied by using sol-gel technique.

Publications

Published:

- W. Pornwannachai, G. Smart, M.H. Akonda, B.K. Kandola, 'The effect of fabric scouring on fire and mechanical performance of flame retarded flax/PP and flax/PLA composites', *Proceeding of the 19th International Conference on Composite Materials (ICCM 19)*, Montreal, Canada, July 2013

In preparation:

- Improvement in fire retardancy of composites by treating fabrics from commingled natural-thermoplastic fibres with various flame retardant
- The influence of surface modification treatments of flame retarded flax/thermoplastic fibres on the fibre/matrix interfacial adhesion of derived composites
- Flame retardant poly(lactic acid) fibres for thermoplastic composites
- Flame retardant furan resins and composites
- Development of flame retardant composites by using different combinations of flame retardant components

Appendix I: Flammability of PLA containing nanoclay and ammonium polyphosphate (APP)

Table I.1: Sample matrix of PLA containing nanoclay and APP

Sample	Additive	Percent mass content (%)	
		Polymer	Additive
PLA+Nanoclay	Nanoclay	98.0	2.0
PLA+APP(2%P)	Ammonium polyphosphate	93.3	6.7
PLA+APP(3%P)		90.0	10.0

Table I.2: Limiting oxygen index (LOI) and UL-94 results of PLA containing nanoclay and APP

Sample	LOI	UL-94 horizontal	UL-94 vertical	
	(%)	B. Rate (mm/min)	B. Rate (mm/min)	V-Rate
PLA	19.9	29.9 ±2.4	68.9 ±4.4	Failed
PLA+Nanoclay	19.7	38.5 ±2.2	103.5 ±8.0	Failed
PLA+APP(2%P)	30.7	-	-	V-0*
PLA+APP(3%P)	31.4	-	-	V-0*

* Sample did not ignite

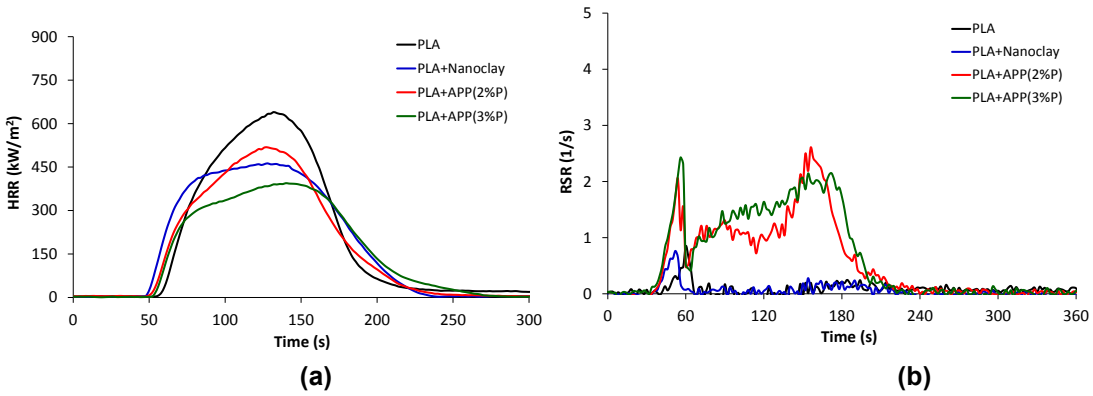

Figure I.1: The cone calorimetric results of PLA containing nanoclay and APP at 35kW/m^2: (a) HRR and (b) RSR curves as a function of time

Table I.3: Cone calorimetric results of PLA containing nanoclay and APP at 35kW/m^2

Sample	TTI (s)	t_{PHRR} (s)	PHRR (kW/m^2)	THR (MJ/m^2)	EHC (MJ/kg)	TSR (L)	Yield (%)
PLA	60 ±3	132 ±1	640 ±2	61 ±1	18 ±1	27 ±8	1.2 ±0.1
PLA+Nanoclays	54 ±1	139 ±1	467 ±21	55 ±2	17 ±1	19 ±9	3.5 ±0.4
PLA+APP(2%P)	56 ±1	127 ±1	520 ±21	52 ±1	17 ±1	190 ±20	5.6 ±0.8
PLA+APP(3%P)	57 ±1	139 ±10	396 ±13	47 ±2	14 ±1	213 ±5	8.6 ±2.9